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ATMOSPHERIC TRANSPORT TO THE GAW REGIONAL STATION AT ZAVIŽAN AND RELATED PRECIPITATION CHEMISTRY

Prijenos onečišćenja na GAW regionalnu postaju Zavižan i kemijski sastav oborine

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Abstract: A study on the connection between the state of the atmosphere, as represented by cluster-mean trajectories, and the chemical composition of precipitation at the Croatian GAW regional station of Zavižan is presented. The trajectory cluster analysis has been done on the basis of daily backward trajectories calculated for 1996, using the HYSPLIT_4 trajectory model. The seasonal cluster analysis indicates four major flow directions in the region: 1) fast W–NW flow, 2) strong SW flow, 3) N–NE flow, 4) very short trajectories of different directions. The major transport route that brings higher levels of acidifying compounds to the region, is from the NW wind sector. The most polluted precipitation has been observed in spring with precipitation connected with three cluster means: NNW, SE and E.

Key words: pollution, air trajectories, cluster analyses

Sažetak: U radu je prikazana analiza veze između stanja atmosfere, reprezentiranog prosječnim putanjama, i kemijskog sastava oborine na GAW postaji Zavižan. Klasterska analiza putanja čestí zraka načinjena je na osnovi dnevnih putanja unatrag proračunatih za 1996. godinu korištenjem modela HYSPLIT_4. Sezonska klasterska analiza pokazuje četiri osnovna smjera strujanja na promatranom području: a) brzo W–NW strujanje, 2) jako SW strujanje, 3) N–NE strujanje, 4) vrlo kratke putanje različitih smjerova. Osnovni smjer prijenosa onečišćenja koji je praćen povećanim količinama komponenti onečišćenja oborine na promatrano područje jest sa NW. Oborina s najvećom količinom onečišćujućih elemenata zabilježena je u proljeće i povezana s tri smjera putanja: NNW, SE i E.

Ključne riječi: onečišćenje, putanje čestí zraka, klasterska analiza

1. INTRODUCTION

The Meteorological Service should serve as a center of activity for the provision of specialized meteorological assistance in the event of large releases of hazardous materials into the atmosphere, such as nuclear or industrial accidents, as well as for regular environmental applications. A flexible environmental modeling and decision support system should be developed to provide tools for use directly by the State and by other institutions engaged in environmental issues, air quality assessment, research, and a variety of other applications.

To study the origin and air/sea exchange of pollutants, it is very important to understand the transport pathways of atmospheric pollutants. A number of methods have evolved to evaluate the transport of pollutants from their source to deposition regions. Complex Eulerian and Lagrangian models are being developed to describe, not only transport itself, but also the chemical processes that take place *en route*. However, the most common method is still the computation of a single back-trajectory to associate the upwind source region with the interpretation of chemical measurements at a given point.

There are frequently clear links between the state of the atmosphere, as represented by different weather patterns, and the composition of precipitation (Smith and Hunt, 1978; Fowler and Cape, 1984; Davies *et al.*, 1984; Davies *et al.*, 1990). The purpose of this paper is to find such links for the GAW and EMEP station at Zavižan in Croatia by analyzing the relationship between daily precipitation chemistry data and cluster-mean trajectories. The clustered trajectories indicate possible sources of pollutant emission and the distribution of weather patterns.

2. DATA AND METHODS

Zavižan, a regional type station, is located in a remote mountain range, 1594 m above sea level (Fig. 1) where no significant changes in land-use practices are taking place or are expected in the future. It is more than 50 km away from major population centers, industrial areas or highways. Effects of natural phenomena, such as forest fires or dust storms, are not experienced at the site. It can be reasonably assumed that the ambient air at the station is entirely free of local pollution and contains only diluted vestiges of chemical components carried to the site by transboundary and long-range transport. Precipitation chemistry data analyses for 12 stations in Croatia (Vidič, 1995) indicate that Zavižan exhibits the lowest major ion concentration values of all sites and therefore is the best choise for monitoring the influence of regional scale pollutants. Surface meteorological observations at the site have been carried out since 1953. The chemical composition of precipitation and the concentrations of reactive gas species, sulphur and nitrogen dioxides, are based on bulk daily sampling. All data are analyzed and stored in the central analytical laboratory at the Meteorological and Hydrological Service in Zagreb.

To study atmospheric transport to Zavižan, three-dimensional 96-h backward isentropic trajectories were computed from 10 m a.g.l.

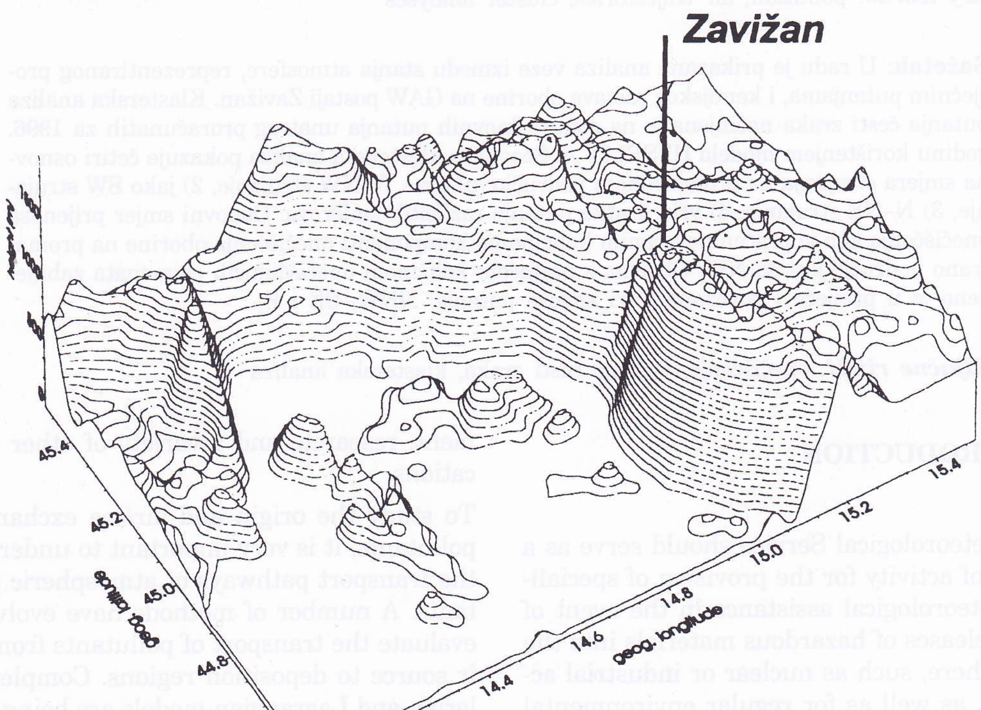

Figure 1. Location of the Zavižan GAW site.

Slika 1. Lokacija GAW postaje Zavižan.

once a day, beginning at 0300 UTC, for the period January–December 1996 using the HYSPLIT_4 (Hybrid Single-Particle Lagrangian Integrated Trajectory) model (Draxler and Hess, 1997). The HYSPLIT_4 model, which can calculate either trajectories or air concentration, is designed for a quick response to atmospheric emergencies, diagnostic case studies, or climatological analyses using previously gridded meteorological data (see web site: *www.arl.noaa.gov/ready.html*). The model calculation method is a hybrid between the Eulerian and Lagrangian approaches. Advection and diffusion calculations are made in a Lagrangian framework while concentrations are calculated on a fixed grid. The advection of a particle is computed independently of the dispersion calculation. The time-integrated advection of each particle can be viewed as a simple trajectory. Meteorological data for the trajectories are obtained from the output fields of a meteorological model. In this case, the gridded meteorological data fields are from the NCEP (National Center for Environmental Prediction) Medium-Range Forecast Model (MRF Archive TD-6140) available from NOAA National Climatic Data Center, Ashville, North Carolina.

In order to group similar trajectories, which indicate similar meteorology, the trajectories have been clustered for each season. Cluster analysis is a common statistical technique of grouping similar objects together to minimize the differences among individual elements in a cluster and maximize the differences between clusters. In the case of trajectories, the goal is for each cluster to represent a different and distinct synoptic regime over the duration of the trajectory. Each cluster should be composed of similar trajectories. Clustering differs from the traditional synoptic classification of weather types because it includes the temporal evolution of the wind fields as opposed to the synoptic classification, which is only valid at a given time. Clustering has been applied to air parcel trajectories to investigate air chemistry (e.g., Moody and Galloway, 1988; Moody and Samson, 1989; Dorling *et al.* 1992) and to develop long-range transport climatology (e.g., Harris, 1992).

The cluster program used for the study has been developed by Stunder (1996) using Ward's method. The cluster variables are the trajectories endpoints, which represent wind speed and direction. Given N trajectories, each is initially defined as a separate cluster with zero spatial variance, where the cluster spatial variance is the sum of the squared distances between the endpoints of the cluster's component trajectories and their (cluster) mean. Successive steps through the clustering process combine the two clusters that result in a minimum increase in total space variance (TSV), where TSV is the sum of all the cluster spatial variances.

In the first several clustering steps, the TSV decreases greatly, then for much of the clustering it typically increases at a small, generally constant rate, but at some point it increases rapidly again, indicating that the clusters being combined are not very similar and therefore all trajectories have been merged into significantly different clusters. At this point the clustering is stopped. The method indicates 5 clusters for each season (example of TSV changes during the clustering procedure for autumn trajectories is given in figure 2).

3. PRECIPITATION REGIME AT ZAVIŽAN

The Zavižan mountain station has the greatest number of days with precipitation and the highest total amount of precipitation in the whole territory of Croatia (Vidič, 1995). The mean annual precipitation amount for 1956–1995 is 1925 mm with a monthly maximum in autumn and a minimum in winter (Fig.3). Although winter has the smallest amount of precipitation per event, the number of days with precipitation is greater than for any other season. Compared to the 40-year mean, 1996 (187 precipitation days with a total precipitation amount of 2156 mm) has a considerably larger number of precipitation days in September and a higher precipitation amount in November. Both months also have a higher number of days with precipitation amounts exceeding 1 mm (Fig. 4). The smallest precipitation amount was observed in March 1996 with only 51 mm in 19 precipitation days compared to 150 mm in 10 precipitation days for the period 1956–1995. The precipitation regime of 1996 was a consequence of different weather characteristics. These weather characteristics can

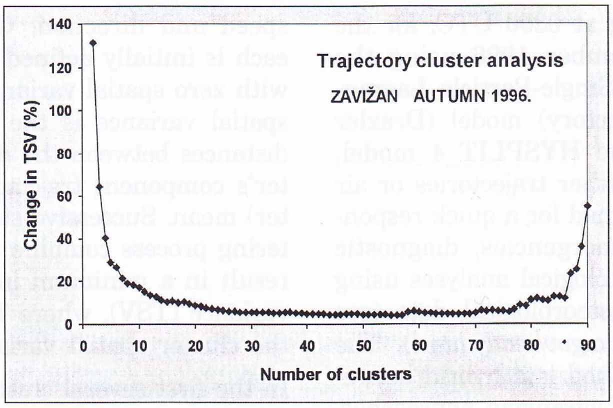

Figure 2. Change in total space variance (TSV in %) during the trajectory clustering procedure for autumn 1996.

Slika 2. Promjena u ukupnoj prostornoj varijanci (TSV u %) tijekom procesa klasteriranja putanja za jesen 1996.

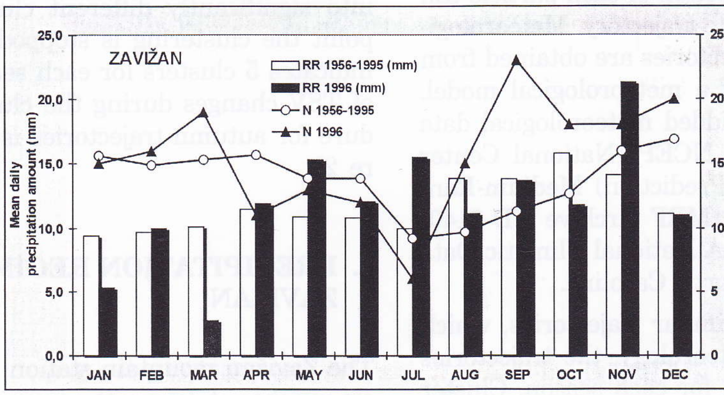

Figure 3. Annual course of mean daily precipitation amount (RR) and mean monthly number of days (N) with precipitation for 1956–1995 and 1996.

Slika 3. Godišnji hod srednje dnevne količine oborine (RR) i srednji mjesečni broj dana s oborinom za 1956–1995. i 1996.

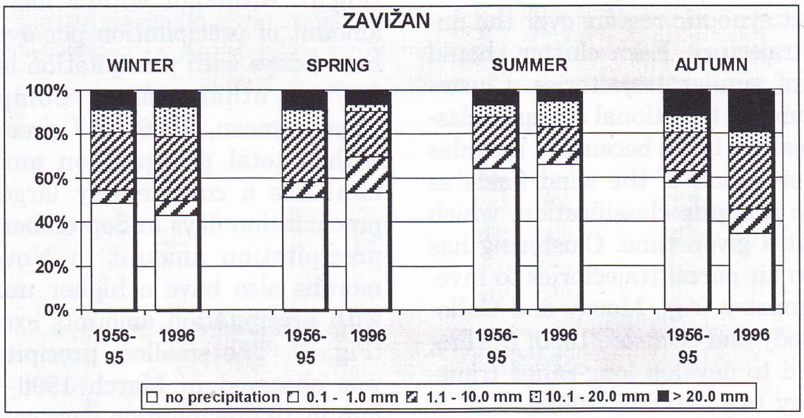

Figure 4. Relative frequencies of the number of days with different precipitation amounts for each season in the periods 1956–1995 and 1996.

Slika 4. Relativna učestalost različite količine oborine za svaku sezonu u razdoblju 1956–1995. i 1996.

be classified by using the trajectory clustering method.

4. RESULTS OF CLUSTER ANALYSIS

The cluster analysis resulted in five cluster-mean trajectories for each season (Fig. 5). Each season is characterized by four dominant regional transport directions (long trajectories) and one cluster that indicates a more local influence (short trajectories within Croatia and neighboring countries). Winter, spring and autumn have the greatest number of trajectories in those short clusters.

In winter, the predominant direction of transport to Zavižan is from SE–NE and the three winter cluster-mean trajectories from those directions contain 80% of all individual trajectories. The autumn cluster-mean trajectories show the predominance of transport form W–NW (common route of frontal systems passing Croatia) and no cluster-mean trajectories go to the northeast. The predominant cluster NNW mean trajectory in spring is much shorter than the typical component trajectory travel distance because the trajectories in that cluster are oriented in many directions (Fig. 6). All other cluster-mean trajectories are more similar to the component trajectories because of the prevalently unidirectional pattern of the trajectories (Fig. 7).

Generally, the seasonal cluster analysis indicates four major weather types in the region:

A) fast W–NW flow connected with frontal passages (trajectories beginning ahead or behind the cold front, where generally strong steady winds are observed that produce a relatively long trajectory) (Fig. 8A);

B) strong SW flow as part of a cyclonic circulation usually centered over Genoa Bay (Fig. 8B);

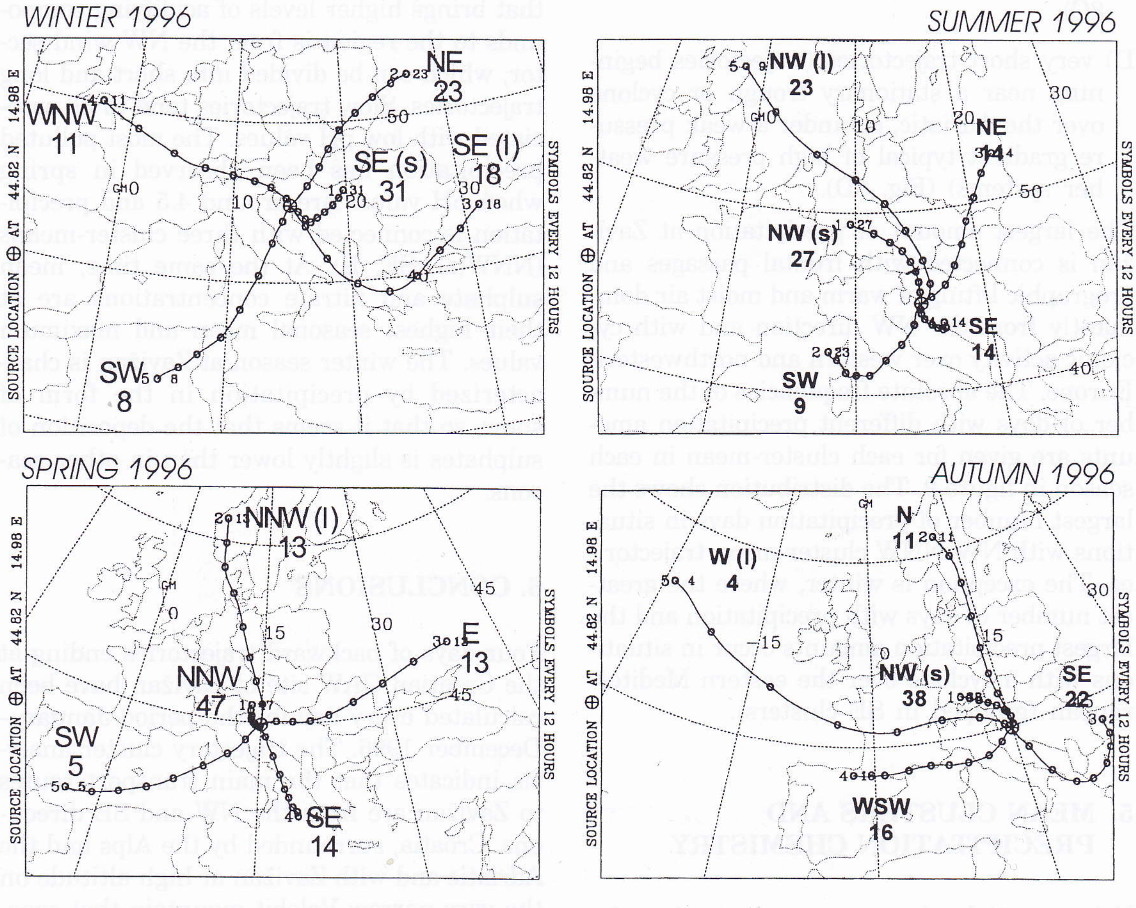

Figure 5. Cluster-mean trajectories for each season.

Slika 5. Srednje putanje čestí zraka za svaku sezonu.

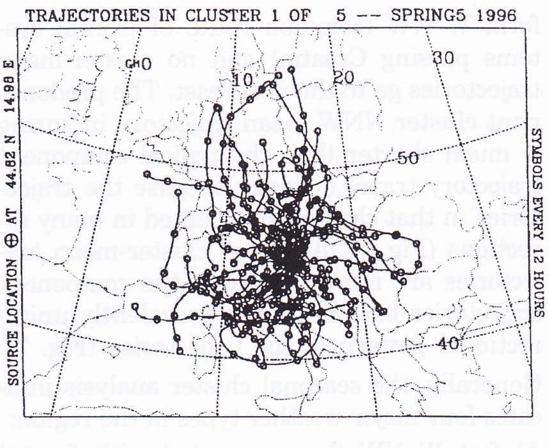

Figure 6. Spring 96-h trajectories ending at Zavižan, composing cluster NNW (s).

Slika 6. 96-satne proljetne putanje čestí zraka koje završavaju na Zavižanu i čine NNW (s) klaster.

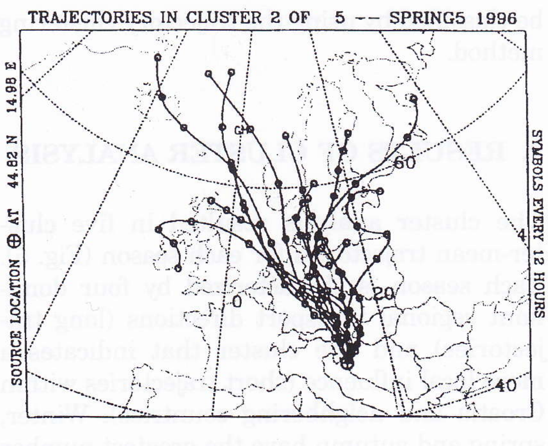

Figure 7. Spring 96-h trajectories ending at Zavižan, composing cluster NNW (l).

Slika 7. 96-satna proljetne putanje čestí zraka koja završavaju na Zavižanu i čine NNW (l) klaster.

C) N–NE flow as part of an anticyclonic system over western or central Europe (Fig. 8C);

D) very short trajectories (trajectories beginning near a stationary trough or cyclone over the Adriatic, or under a weak pressure gradient typical of high pressure weather systems) (Fig. 8D).

The largest amount of precipitation at Zavižan is connected with frontal passages and orographic lifting of warm and moist air dominantly from the NW direction and with cyclonic activity over western and northwestern Europe. The absolute frequencies of the number of days with different precipitation amounts are given for each cluster-mean in each season in figure 9. The distribution shows the largest number of precipitation days in situations with NW–NNW cluster-mean trajectories. The exception is winter, where the greatest number of days with precipitation and the largest precipitation amounts occur in situations with a cyclone over the eastern Mediterranean (grouped in SE clusters).

5. MEAN CLUSTERS AND PRECIPITATION CHEMISTRY

Volume weighted average concentrations for major ions and pH have been calculated for each cluster within the season in order to relate atmospheric transport paths to the precipitation chemistry at Zavižan (Tab. 1). The results show that the major transport route that brings higher levels of acidifying compounds to the region is from the NW wind sector, which can be divided into short and long trajectories. Slow trajectories tend to be associated with low pH values. The most polluted precipitation has been observed in spring when pH values are around 4.5 and precipitation is connected with three cluster-means (NNW(s), SE, E). At the same time, mean sulphate and nitrate concentrations are at their highest seasonal mean and maximum values. The winter season at Zavižan is characterized by precipitation in the form of snow, so that it seems that the deposition of sulphates is slightly lower then in other seasons.

6. CONCLUSIONS

Four days of backward trajectories ending at the Croatian GAW site of Zavižan have been calculated every day for the period January–December 1996. The trajectory cluster analysis indicates that the main transport routes to Zavižan are from the NW and SE directions. Croatia, surrounded by the Alps and the Adriatic and with Zavižan at high altitude on the very narrow Velebit mountain that separates the coast from the inland area.

Although the relation between the transport paths and precipitation chemistry provides

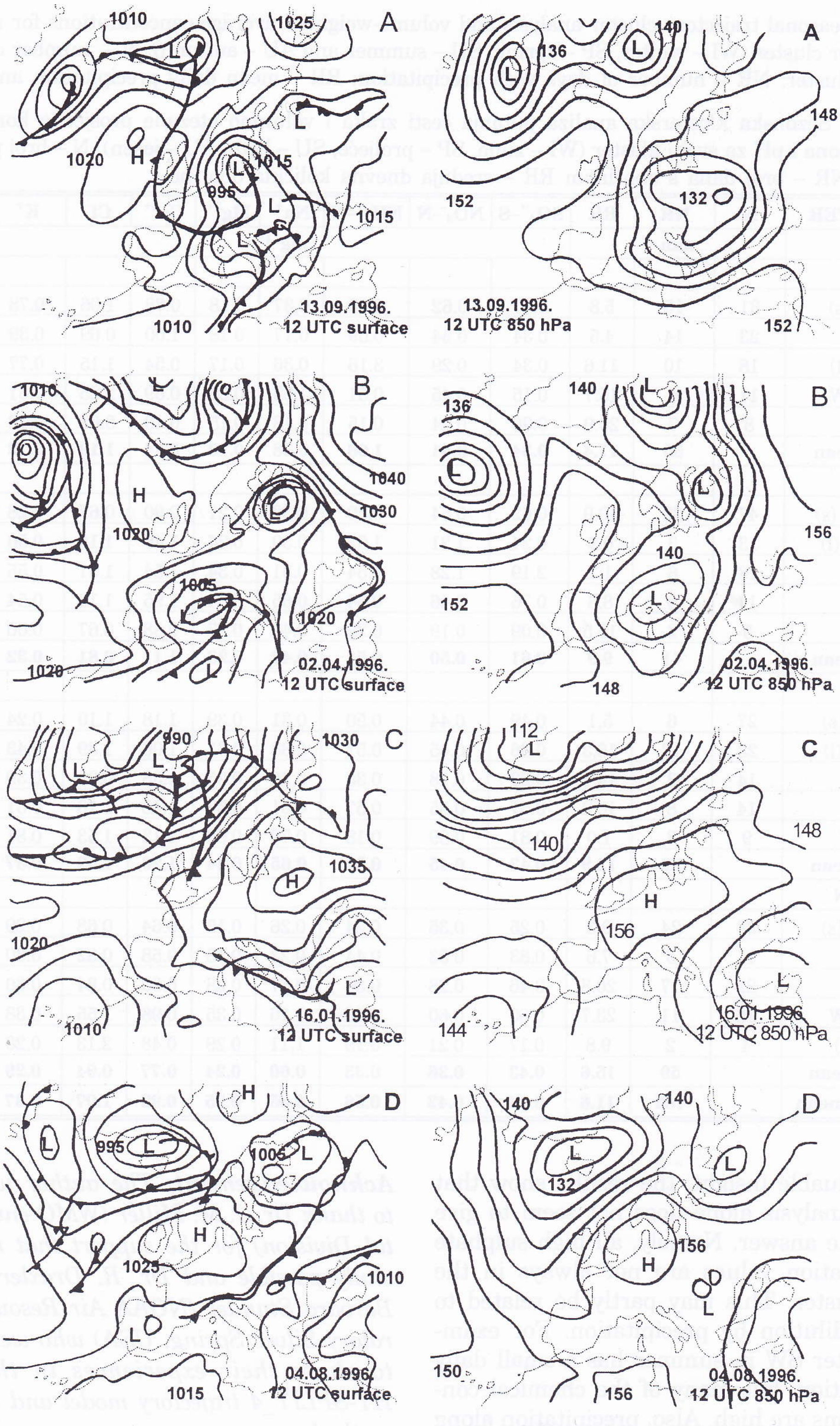

Figure 8. Examples of surface (left) and AT 850 hPa (right) synoptic situations at 12 UTC for major weather types in the Zavižan region. A) fast W–NW flow, B) strong SW flow, C) N–NE flow, D) weak pressure gradient situation.

Slika 8. Primjeri prizemne (lijevo) i AT 850 hPa (desno) sinoptičke situacije u 12 UTC za osnovne tipove vremena na području Zavižana: A) brzo W–NW strujanje, B) jako SW strujanje, C) N–NE strujanje, D) situacija sa slabim gradijentom tlaka.

Table 1. Seasonal trajectory cluster analysis and volume-weighted average concentrations for major ions and pH per cluster (WI – winter, SP – spring, SU – summer and AU – autumn). N – number of trajectories per cluster; NR – number of days with precipitation; RR – mean daily precipitation amount.

Tablica 1. Sezonska klasterska analiza putanja čest i zraka i volumno otežane prosječne koncentracije osnovnih iona i pH za svaki klaster (WI – zima, SP – proljeće, SU – ljeto, AU – jesen). N – broj putanja po klusteru NR – broj dana s oborinom RR – srednja dnevna količina oborine.

CLUSTER	N	NR	RR	$SO_4^{=}$-S	NO_3^--N	NH_4^+-N	Na^+	Mg^{2+}	Ca^{2+}	Cl^-	K^+	pH
			mm				$mg\ l^{-1}$					pH un.
WINTER												
SE (s)	31	15	5.8	0.37	0.62	0.65	0.37	0.18	0.78	1.06	0.78	4.75
NE	23	14	4.5	0.34	0.54	0.59	0.17	0.18	1.00	0.69	0.39	4.93
SE (l)	18	10	11.6	0.34	0.29	3.16	0.36	0.17	0.54	1.15	0.77	5.12
WNW	11	4	15.7	0.15	0.45	0.51	1.63	0.26	0.69	2.25	0.61	5.31
SW	8	7	20.9	0.30	0.24	0.15	0.18	0.15	0.49	0.68	0.12	5.80
WI mean		**50**	**11.4**	**0.34**	**0.41**	**1.08**	**0.48**	**0.19**	**0.74**	**1.19**	**0.72**	**5.08**
SPRING												
NNW (s)	47	22	10.9	0.62	0.54	0.50	0.36	0.21	0.90	0.67	0.28	4.59
NNW(l)	13	3	0.2	0.24	1.21	1.03	0.30	0.24	1.49	1.15	0.50	6.57
t E	13	6	1.7	2.19	1.28	1.54	0.51	0.34	1.54	1.91	0.55	4.80
SE	14	8	8.8	0.76	0.46	0.54	0.65	0.34	1.95	1.13	0.54	4.40
SW	5	2	15.5	0.09	0.19	0.29	0.42	0.17	0.58	0.67	0.00	5.97
SP mean		**41**	**9.9**	**0.61**	**0.50**	**0.51**	**0.42**	**0.23**	**1.11**	**0.81**	**0.32**	**4.60**
SUMMER												
NW (s)	27	6	5.1	0.49	0.44	0.50	0.31	0.39	1.18	1.10	0.24	6.21
NW (l)	23	12	16.3	0.36	0.45	0.51	0.88	0.31	1.06	1.89	0.43	5.96
NE	14	3	14.1	0.23	0.18	0.35	0.26	0.25	1.38	0.93	0.39	6.60
SE	14	8	16.6	0.57	0.55	0.57	0.51	0.37	1.48	1.18	0.31	6.23
SW	9	3	1.0	0.81	0.89	0.18	0.79	0.98	4.13	1.53	0.81	6.82
SU mean		**32**	**12.9**	**0.43**	**0.45**	**0.51**	**0.65**	**0.34**	**1.26**	**1.49**	**0.37**	**6.10**
AUTUMN												
NW (s)	38	24	9.3	0.25	0.35	0.24	0.26	0.13	0.64	0.68	0.29	4.89
N	11	5	7.6	0.83	0.53	0.44	0.23	0.18	0.58	0.32	0.30	5.39
SE	22	17	20.8	0.46	0.28	0.36	0.57	0.28	0.90	0.84	0.30	5.20
WSW	16	11	23.7	0.60	0.60	0.46	1.16	0.35	0.98	1.55	0.38	5.09
W(l)	4	2	9.8	0.17	0.21	0.15	1.11	0.29	0.48	2.13	0.20	6.57
AU mean		**59**	**15.6**	**0.43**	**0.36**	**0.33**	**0.60**	**0.24**	**0.77**	**0.94**	**0.29**	**5.12**
Annual mean		**182**	**11.6**	**0.44**	**0.42**	**0.56**	**0.55**	**0.25**	**0.92**	**1.07**	**0.37**	**5.02**

some valuable insight, the results show that cluster analysis alone does not seem to give the whole answer. Namely, all high sulphate concentration values are not always in the same cluster. This may partly be related to sample dilution by precipitation. For example, cluster SW in summer has a small daily precipitation, but many of the chemical concentrations are high. Also, precipitation along the transport path may „deplete" the sample.

Using a longer period of data, the techniques used in this study, may be applied to develop climatologies for Zavižan and other sites where there is a need to identify common flow patterns and potential source regions.

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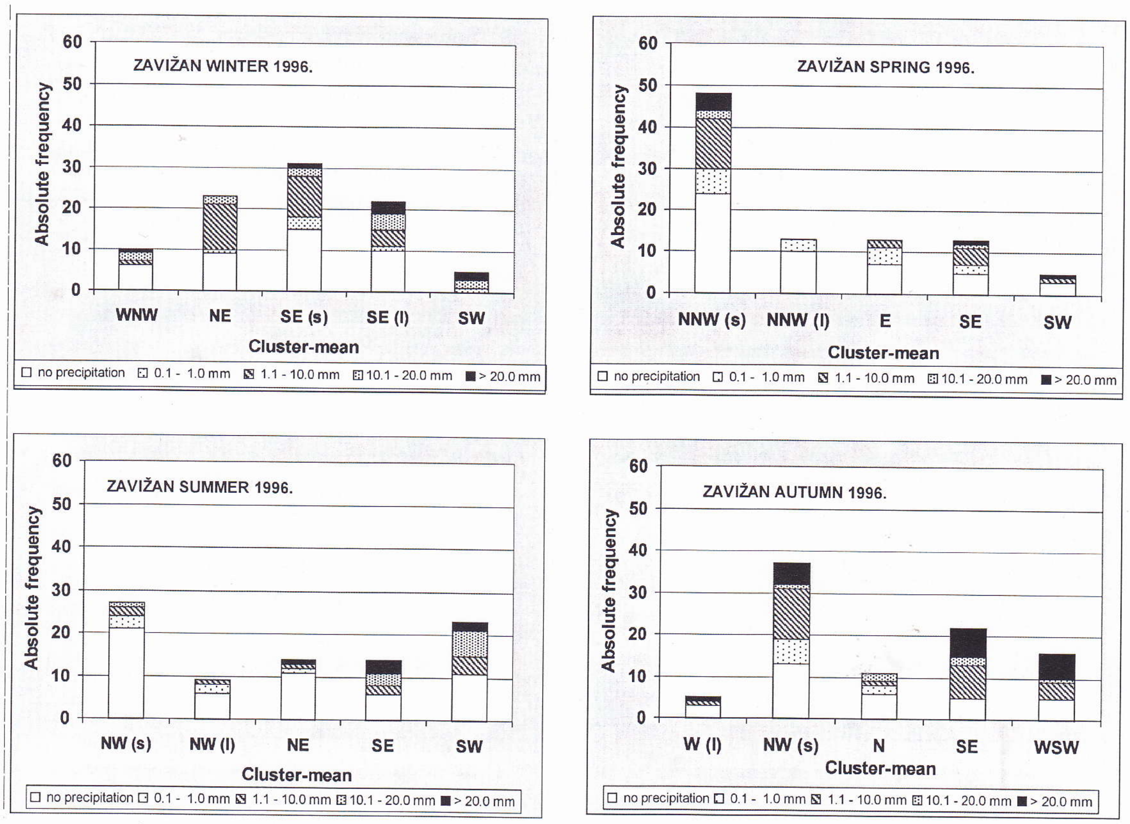

Figure 9. Absolute frequencies of precipitation days with different amount of precipitation for each cluster-mean in each season.

Slika 9. Apsolutne čestine dana s oborinom s različitom količinom oborine za svaki sezonski prosječni klaster.

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