Major ions wet deposition and trends during the last decade on the eastern Adriatic coast

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Abstract

The Croatian Adriatic coast is under the combined influence of local, regional and long-distance pollution sources. Wet deposition of atmospheric pollution contributes to an ecological imbalance of the whole ecosystem, including the sea itself. The Adriatic is ecologically very sensitive, because of its geographic position, complex orography, specific meteorological conditions and number of pollution sources. Predominant airflow is land to sea. The precipitation amount is high in the area of the highest air pollution, which results in high wet deposition. The purpose of this paper is to evaluate the load of the Adriatic Sea and coast by atmospheric pollution. For that purpose, the deposition of major ions in bulk daily precipitation samples was examined at five stations along the eastern, Croatian, Adriatic coast over the last 10 years (2001–2010). Results were compared with the previous period in order to evaluate possible trends.
Keywords: wet deposition, Adriatic coast, trend.

1 Introduction

Precipitation is important for life and for replenishing ground and surface water. Therefore, precipitation chemistry monitoring is important for human environment protection. The emission of pollutants into the atmosphere originates from different human activities such as industry, agriculture, inappropriate waste treatment, etc. Air pollution monitoring and its result is a strong tool for policy makers in pollutant emission control.

The Adriatic Sea is ecologically very sensitive, because it is a semi-enclosed sea and because of its geographic position, complex orography, specific meteorological conditions and number of pollution sources. Economical loss

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caused by environmental pollution, especially in tourism which is one of the most important income sources for Croatia, is important too.

In Croatia, the Meteorological and Hydrological Service (DHMZ) has been monitoring and researching atmospheric precipitation quality and air pollution since the early eighties of the last century. Bulk daily precipitation samples are analysed for major ions: pH, sulphates, nitrates, chlorides, ammonium, potassium, calcium, sodium and magnesium. The chemical composition of precipitation in Croatia is, as everywhere in the world, the result of the combined influence of natural and anthropogenic sources from local, regional and long-distance emission sources. Some of the most important sources, recognized in different scientific research papers, are the Adriatic Sea, forest fires, local transport, construction work, Saharan dust, local, regional and long-distance industry, volcano eruptions, agricultural activities including animal breeding and tourism (Bajic and Djuricic [1], Vidic [2], Alebic-Juretic and Sojat [3], Sojat *et al*. [4], Pozar-Domac *et al*. [5], Sojat and Borovecki [6], Spoler Canic *et al*. [7]).

The purpose of this paper is to evaluate the load of the Adriatic Sea and coast by atmospheric pollution. For that purpose, the deposition of major ions in bulk daily precipitation samples was examined at five stations along the eastern, Croatian, Adriatic coast during the last 10 years (2001–2010). This is the period in which the last war in Croatia (1991−1995) and the reconstruction was over, but also the period of the decreasing industry activities and the beginning of the recession and economic crisis.

Research presented in this paper will be continued by detailed investigation of meteorological parameters closely connected to precipitation composition (wind sector analysis, precipitation regime analysis, trajectory analysis).

2 Material and methods

2.1 Study area

Five stations on the Adriatic coast considered in this paper (figure 1) belong to the monitoring network of precipitation chemistry, established and maintained by the Meteorological and Hydrological Service of Croatia (DHMZ). All of them are located at meteorological stations.

Rijeka (φ=45° 20′N, λ=14° 27′E, h=120 m asl) is the largest Croatian shipyard and harbour on the Adriatic coast, situated in the Kvarner Bay in the Northern Adriatic. In addition, a great number of pollution sources are assembled here: an oil refinery and petroleum industry, a cokery, a thermal power plant, local industries, heavy traffic, domestic heating. The meteorological station is situated on a hill slope in the northern part of the city, about 2 km from the city centre. The station is under the influence of local and regional pollution sources, but emission of pollution from the above mentioned local sources was decreased in the considered period, compared to the period before 1991.

Zadar (φ=44° 8′N, λ=15° 13′E, h=5 m asl) is in the mid Adriatic. Local pollution sources in Zadar are from local industry (sawing machines, foodstuff), traffic and, in a small amount, domestic heating. The meteorological station is in the suburb, about 50 m from the sea, under the sea's influence.

Figure 1: Sampling sites for precipitation quality on the Croatian Adriatic coast which are considered in this paper.

Split–Marjan (φ=43° 31′N, λ=16° 26′E, h=122 m asl) is in the mid Adriatic too, to the south of Zadar. Split is the biggest Croatian coastal city. Local pollution sources are road and sea traffic, domestic heating, some industry (engine, tools and machines, electrical equipment, shipyard, harbour). The meteorological station is situated in the recreation zone on the hill Marjan, in the north-western part of the city, near the zoo and in pine forest surroundings.

Dubrovnik (φ=42° 39′N, λ=18° 5′E, h=52 m asl) is a southern Adriatic station. It is open to the sea in all directions except to the west, and under the strong sea influence, especially affected by *jugo,* a strong southern wind. There are no significant anthropogenic pollution sources in the region.

Komiza (φ=43° 3′N, λ=16° 6′E, h=20 m asl) is the station in a small fishing village, on the island of Vis in the southern Adriatic. This offshore monitoring site is open to the sea from all three directions and under the strong sea influence, especially affected by *jugo,* a strong southern wind. There are no significant anthropogenic pollution sources in the region. Residents occasionally dispose of building materials close to the station.

2.2 Sampling and analysis

The daily bulk precipitation samples are collected in open polyethylene buckets in accordance with the precipitation measurement protocol; from 07 to 07 CET. Samples are transported to the laboratory twice a month. All samples are analysed in the chemical laboratory of the DHMZ, according to EMEP manual (EMEP-CCC Report [8]).

Radiometer PHM93 pH-meter with glass electrodes is used for pH measurements. The radiometer CDM 210 conductivity-meter is used to determine electric conductivity of the samples. Major ions are determined by ion chromatography: chlorides, nitrates and sulphates on Dionex DX 500, while ammonium, sodium, potassium, calcium and magnesium on Dionex ICS 1000.

2.3 Data quality control

The accuracy of analytical results is ensured by participation in interlaboratory comparisons organized by EMEP, GAW, the International School of Ion Chromatography and the NEU project.

The consistency of the samples is checked by ion balance and by comparison of calculated and measured electrical conductivities. The ion balance is calculated for every single sample.

2.4 Trend and time series analysis

The existence of a trend in the annual ion wet deposition was tested using the nonparametric Mann-Kendall test. This test is often used in precipitation chemistry analysis because the data do not need to conform to any particular distribution and missing values are allowed. Since this test does not estimate a trend slope, the slope was estimated by means of the nonparametric Sen's method, which uses a linear model. The Sen's slope estimator is the median of the slopes calculated from all pairs of values in the data series. The trends were tested at four levels of significance: $\alpha = 0.001$, 0.01, 0.05 and 0.1. The Sen's estimator was calculated for a time series with a trend significant at least at $\alpha = 0.05$ and for the time series with 10 results. The results were obtained using MAKESENS software (Salmi *et al.* [9]).

3 Results and discussion

Precipitation regime in Croatia is the consequence of passing cyclones and related atmospheric fronts, within the general circulation of the atmosphere. It results with more precipitation in summer in the northern Adriatic coast while going toward south-east the frontal systems become weaker and give less precipitation. During autumn and early winter, a great number of circulation systems pass over Mediterranean and Adriatic Sea toward the inland. Moisture-bearing maritime air masses face extremely developed orography of Dinarides which force air masses to lift, resulting in condensation, convective cloudiness and precipitation.

In the period 2001–2010 northern (Rijeka) and southern (Dubrovnik) Adriatic get about 70% more precipitation than mid Adriatic (table 1, figure 2). However, number of precipitation days is the greatest in Rijeka, which means that precipitation events with greater precipitation amount are more often in the south. This is mainly due to summer rain showers. Mean annual precipitation amounts in the period 2001–2010 compared with the climate period 1971–2000, (Zaninovic *et al.* [10]) show a little bit less precipitation in the north (Rijeka: 98%, Zadar: 97%), and more in the south (Split: 110%, Dubrovnik: 113%).

Efficiency is 91–99%, mainly due to samples with a small amount of rain, not enough for chemical analysis.

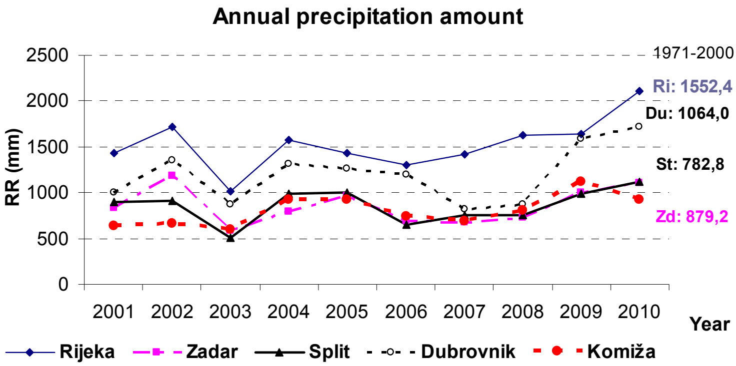

Figure 2: Annual precipitation amount for selected stations on the Adriatic coast in the period 2001–2010.

Table 1: Statistic parameters of analyzed precipitation for the period 2001–2010.

Parameter	Rijeka	Zadar	Split	Dubrovnik	Komiza
N	1106	963	964	894	784
RRtot. (mm)	15272.2	8591.0	8588.6	12016.4	8049.5
Efficiency (%)	98.9	98.6	98.0	97.7	98.4
pHmin	3.28	4.24	4.64	4.27	3.94
pHmax	8.74	9.80	7.91	8.06	8.06

(N = number of samples, RRtot. = total precipitation amount for the whole period, Efficiency = chemically analyzed precipitation amount in mm divided by total precipitation amount in mm (expressed in %), pHmin = minimum pH value in daily sample, pHmax = maximum pH value in daily sample).

Acidity of precipitation is not such a big issue as it was in the last three decades of the last century. Percentage of acid rain varies between 3 and 45% for all stations except Rijeka, where it varies between 20 and 50%. However, individual samples can still be very acid (pHmin, table 1), but also very basic (pHmax). Since detailed analysis of precipitation pH value was not the issue of this paper, the highest and the lowest pH values shown here are only for basic information.

3.1 Wet deposition

Annual wet deposition is calculated as the product of volume weighted annual mean concentration of the particular ion and total annual precipitation amount. Annual wet deposition of major ions in precipitation for five stations on the Adriatic coast, in the period 2001–2010 is shown in figure 3. Note that the scale is different for different ions.

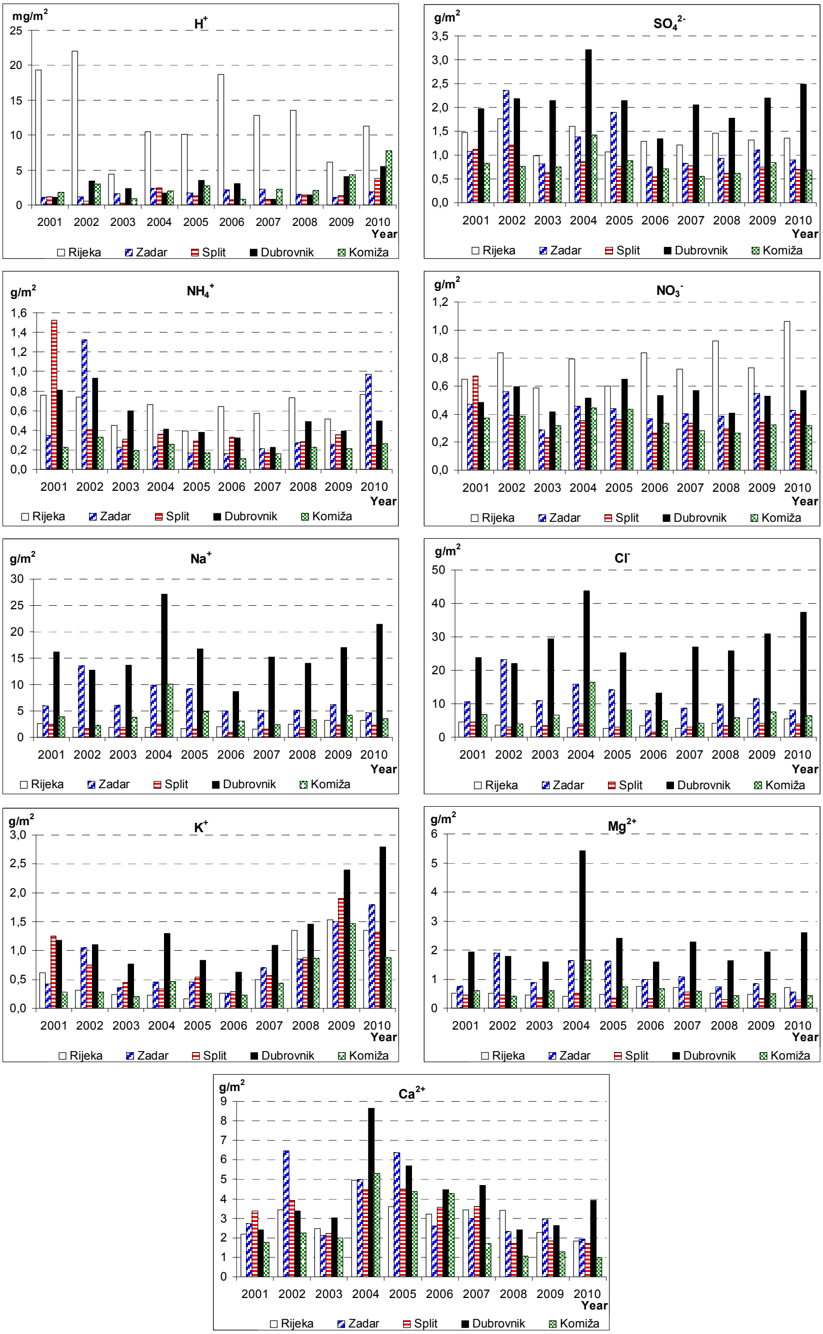

Figure 3: Annual wet deposition of major ions in precipitation at selected sites on the Adriatic coast, period 2001–2010.

It is obvious that among all stations Dubrovnik is under the strongest sea influence, since it has the highest deposition rate of sodium, chlorides, sulphates and magnesium. Zadar and the offshore station Komiza are also under strong sea influence, but the precipitation amount at these stations is much lower than in Dubrovnik, so the deposition is lower too. The mean annual deposition of ions that indicate sea influence is on average 8 to 9 times higher in Dubrovnik than at sites with the lowest deposition. Deposition of sodium varies from 1.9 gm^{-2} in Split to 7.1 gm^{-2} in Zadar, while in Dubrovnik it is 17.6 gm^{-2}. The mean annual deposition of chlorides varies even more. It is the smallest in Rijeka (3.8 gm^{-2}) and Split (3.4 gm^{-2}), double at the island station Komiza (7.1 gm^{-2}), 12.1 gm^{-2} in Zadar, while in Dubrovnik it is more than double of that in Zadar (29.6 gm^{-2}). Deposition of magnesium varies from an average yearly value of 0.4 gm^{-2} in Split to 2.7 gm^{-2} in Dubrovnik.

Acid deposition is the highest in Rijeka, as well as the deposition of nitrates. As we have mentioned in section 2.1, among considered stations, Rijeka is under the strongest influence of local industry and heavy traffic.

Besides nitrates, sulphates contribute the most to the precipitation acidity and they also indicate anthropogenic (mainly industrial) pollution sources. Deposition of sulphates in all years except in 2002 is the highest in Dubrovnik, but this is because of the natural source (sea spray). It has to be mentioned here that we did not correct sulphate concentrations for the contribution of the sea salt for any of the stations considered. If Dubrovnik is neglected, the highest sulphate deposition is in Rijeka (northern Adriatic) and Zadar (mid Adriatic), two cities with local industrial and traffic pollution sources. At first glance, it may be surprising that Split, the biggest city on the coast, does not have such high sulphate and nitrate deposition. This can be explained with the micro-location of the sampling site; it is in a recreational zone, on a hill above the city centre.

Wet deposition of hydrogen, sulphur and nitrogen has decreased a lot in the last two decades (Djuricic *et al.* [11], Vidic [2]). Compared to the period 1981–1992 (Vidic [2]) long-term average values for the period 2001–2010 are lower between 60% (nitrates in Dubrovnik) and 160% (hydrogen in Zadar). As discussed in Spoler Canic *et al.* [7] Croatian SO_2 and NO_2 emissions began to decrease after 1990. The reduction in emissions emerged because of two major factors. One is the decline in industrial and energy consumption generated by the Homeland War, the other is the economical transition processes that occurred at the beginning of 1990s. The latter is in accordance with the high SO_2 and NO_2 emission reduction in the whole of Central and Eastern Europe between 1990 and 1999. Reduction in emissions in Croatia as well as in Europe has continued in the last decade due to the recession.

Ammonia is a reactive pollutant emitted primarily by agricultural sources near ground level in rural environments, and it has a major impact on a local scale. It would be expected that ammonium deposition is the highest in Zadar, with the agricultural areas in the hinterland. However, this happened only in 2002 and 2010, while in the period from 2004 to 2009 ammonium deposition was the highest in Rijeka. This might be explained by the fact that precipitation occurs in Zadar mainly with the air masses arriving from the sea, not from inland, while in Rijeka ammonia sources might be the oil refinery and petroleum industry. However, ammonia wet deposition has decreased 40% to 190% compared with previous periods (Djuricic *et al.* [11], Vidic [2]).

Calcium shows mainly the influence of anthropogenic sources, such as sea salt, soil erosion, forest fires, Saharan dust and volcanic eruptions, while anthropogenic sources include dust from unpaved roads, quarrying and construction works. Deposition of calcium in the period 2001–2010 was on average from 2.5 gm^{-2} in Komiza to 4.8 gm^{-2} in Dubrovnik, but varied quite a lot from year to year. In some years it was the highest in Dubrovnik, in other in Zadar, or Split, or Rijeka. Generally, it was the highest in 2004 with a decreasing trend after that.

Annual deposition of potassium was below 1 gm^{-2} for all stations except Dubrovnik till 2007 when an increasing trend started for all stations.

The annual deposition of magnesium is below 1 gm^{-2} in Rijeka, Split and Komiza, and between 1 and 2.7 gm^{-2} in Zadar and Dubrovnik. We cannot find an explanation for the peak in Dubrovnik in 2004 in deposition of magnesium, but also sodium, chloride, sulphate and calcium.

3.2 Trend analysis

Table 2 shows mean annual precipitation, average deposition of major ions and trend statistics at the studied monitoring sites for the period 2001–2010.

Most of the components did not show any significant trend (precipitation, annual deposition of hydrogen, chloride, sulphate, nitrate and sodium ion) at any site.

Deposition of ammonium ion had a decreasing trend at sites Dubrovnik and Split, but the significance level was low: 0.05 for Split and 0.1 for Dubrovnik. At the rest of the sites the trend was not significant.

Annual deposition of potassium ion increased in Zadar and Dubrovnik. At both sites significance level was 0.05. At all the other sites the trend was not significant.

Deposition of calcium ion was slightly decreased in Komiza (level of significance was 0.1), and at the other sites it was without significance.

About deposition of magnesium ion: at sites Split and Komiza it showed a decreasing trend (significance level was 0.1). Again, all the other sites showed no significant trend.

4 Conclusions

Analysis of wet deposition of major ions in precipitation for the period 2001–2010, comparing with results of some previous research and trend analysis results in several conclusions:

– The Croatian Adriatic coast is under the combined influence of local, regional and long-distant anthropogenic pollution sources and natural sources.

Table 2: Mean annual precipitation and average wet deposition of major ions at the studied monitoring sites 2001–2010.

ID	Site	Average deposition	Trend significance	Est.	Min.	Max.
Precipitation, mm						
1	Rijeka	1527.22	n.s			
2	Zadar	859.10	n.s			
3	Split	858.86	n.s			
4	Dubrovnik	1201.64	n.s			
5	Komiza	832.70	n.s			
H^+, *mg/m²*						
1	Rijeka	12.549	n.s			
2	Zadar	1.656	n.s			
3	Split	1.383	n.s			
4	Dubrovnik	2.696	n.s			
5	Komiza	2.750	n.s			
Cl^-, *g/m²*						
1	Rijeka	3.817	n.s			
2	Zadar	12.071	n.s			
3	Split	3.406	n.s			
4	Dubrovnik	29.681	n.s			
5	Komiza	7.089	n.s			
SO_4^{2-}*-S, g/m²*						
1	Rijeka	1.375	n.s			
2	Zadar	1.201	n.s			
3	Split	0.799	n.s			
4	Dubrovnik	2.295	n.s			
5	Komiza	0.805	n.s			
NO_3 *-N, g/m²*						
1	Rijeka	0.798	n.s			
2	Zadar	0.434	n.s			
3	Split	0.365	n.s			
4	Dubrovnik	0.538	n.s			
5	Komiza	0.347	n.s			
NH_4^+*-N, g/m²*						
1	Rijeka	0.622	n.s.			
2	Zadar	0.417	n.s.			
3	Split	0.426	*	20	-101	-1.8
4	Dubrovnik	0.497	+	51	-1192	1995
5	Komiza	0.214	n.s.			

Table 2: Continued.

ID	Site	Average deposition	Trend significance	Est.	Min.	Max.
Na^+, g/m²						
1	Rijeka	2.255	n.s			
2	Zadar	7.071	n.s			
3	Split	1.900	n.s			
4	Dubrovnik	17.605	n.s			
5	Komiza	4.138	n.s			
K^+, g/m²						
1	Rijeka	0.652	n.s.			
2	Zadar	0.784	*	98	-12	264
3	Split	0.825	n.s.			
4	Dubrovnik	1.337	n.s.			
5	Komiza	0.531	*	83	-3.2	184
Ca^{2+}, g/m²						
1	Rijeka	3.083	n.s			
2	Zadar	3.541	n.s			
3	Split	3.089	n.s			
4	Dubrovnik	4.750	n.s			
5	Komiza	2.503	+	179	-740	171
Mg^{2+}, g/m²						
1	Rijeka	0.553	n.s			
2	Zadar	1.101	n.s			
3	Split	0.389	+	-17	-35	0.7
4	Dubrovnik	2.699	n.s			
5	Komiza	0.660	+	-25	-80	15

Trend significance: *, $\alpha = 0.05$ and +, $\alpha = 0.1$. Sen's slope estimate EST. (in g/m^2yr) with its 95% confidence interval (Min., Max.), n.s.= not significant.

- The wet deposition of hydrogen, sulphur and nitrogen (from nitrates and ammonia) has decreased in the last two decades by factors from 1.6 to 2.9.
- Ammonium ion deposition had a decreasing trend in the mid Adriatic (Zadar) and southern Adriatic (Dubrovnik) area, as it was with calcium (in Komiza) and magnesium (in Split). Significance levels were 0.05–0.1. Only potassium ion showed an increasing trend (Zadar, Komiza), with significance level 0.05. The rest of the ions did not show any significant trend.

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