

SHORT COMMUNICATION

CHEMICAL COMPOSITION OF RAINWATER COLLECTED AT TWO SAMPLING SITES IN THE CITY OF RIJEKA

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This study compares the chemical composition of rainwater samples collected at two sampling sites, the first situated in the Rijeka city centre and the second in a suburban site 120 m above the sea level. The rainwater samples were analysed for precipitation weighted average concentrations of hydrogen, sulphate, nitrate, chloride, ammonium, sodium, potassium, calcium, and magnesium. The results suggest that the local washout of the atmosphere enhanced the rainwater acidity in the city centre which also received significant marine contributions of sulphate, calcium, magnesium, and potassium content. Rainwater in the suburban site was affected by soil dust and/or fertilizers used in the nearby gardens, resulting in partial neutralization with rising of pH value. While the content of S-SO₄ was practically equal at both sites, the quantities of N-NO₃ and N-NH₄ nearly doubled at the suburban site.

Key words:
acid precipitation, precipitation chemistry, sea salt, urban effects, wet deposition

Sampling sites selected for the monitoring of long-range transport of pollutants, that is, of precipitation chemistry, are usually distant from urban areas. The intention is to collect samples representative of given meteorological conditions and of the distribution of emission sources. While such measurements are useful and required in many predictions such as the estimation of damages caused by acid precipitations on buildings, cultural heritage, and ecosystems, as well as the estimation of regional contribution to national wet deposition, literature gives little data concerning precipitation chemistry in urban areas (1).

The first analyses of rainwater samples in the Rijeka city area began in the mid-eighties at two sampling sites, one monitored by the Meteorological and Hydrological Service of Croatia (2) and the other by the Institute of Public Health in Rijeka (3). The aim of this study was to compare the chemical composition of rainwater samples collected at both sampling sites in the period between April 1990 and May 1991.

MATERIALS AND METHODS

Figure 1 shows the positions of the two sampling sites. Site 1, monitored by the Institute of Public Health, is located in the city centre, on the terrace of the Institute building, approximately 30 m above a busy street, separating the harbour from the residential area, and approximately 100 m away from the sea. Site 2, monitored by the Meteorological and Hydrological Service of Croatia, is in a suburban field 120 m above the sea level. The sampler is mounted at 1.5 m above the ground. The distance between the two sites is about 1400 m and both may be considered urban.



Figure 1 Locations of the two sampling sites in the city of Rijeka:
Site 1 – City centre (ref. 3), Site 2 – Suburban area.

Daily rainwater samples were collected in the open polyethylene buckets using the so called »bulk« method. According to literature, the contribution of dry deposition in »bulk« samples may reach up to 20% (4). After the collection and determination of pH values, the samples were stored in a refrigerator until the analyses on sulphate, nitrate, chloride, ammonium, calcium, magnesium, potassium and sodium content. The methods used for the rainwater analysis were identical in both institutions, save for ammonium which was analysed with a spectrophotometer at the Institute of Public Health, and with ion-selective electrode at the Meteorological and Hydrological Service of Croatia. Sulphates were determined turbidimetrically with BaCl₂. Chlorides were analysed with ion-selective electrode, while concentrations of nitrate and ammonium were determined spectrophotometrically. Concentrations of sodium, potassium, calcium, and magnesium were determined by flame atomic absorption spectrometry. All those methods were used in the analysis of rainwater samples carried out within the European Monitoring and Evaluation Programme (5).

RESULTS AND DISCUSSION

Table 1 shows the results of rainwater analyses for the period March 1990–May 1991. Although nearly twice as much rainwater samples were collected at Site 2 as at Site 1, the overall precipitation volumes were similar at both sites due to the fact that the precipitation depth in 43 samples collected at Site 2 varied between 1 and 8 mm and the precipitation volume was 175.6 mm (14.5% of total volume). The number of

Table 1 *Precipitation weighted average concentrations of main ions in rainwater samples (µM)*

Parameter	Site 1 City centre (ref. 3)	Site 2 Suburban area
[H ⁺]	31	18
[SO ₄ ²⁻]	54	51
Non sea-salt-[SO ₄ ²⁻]	37	–
[NO ₃ ⁻]	49	77
[NH ₄ ⁺]	79	151
[Cl ⁻]	61	67
[K ⁺]	5	28
Non sea-salt-[K ⁺]	4	–
[Ca ²⁺]	26	53
Non sea-salt-[Ca ²⁺]	21	–
[Mg ²⁺]	14	41
Non sea-salt-[Mg ²⁺]	2	–
[Na ⁺]	67	103
pH (median)	4.9	5.76
V (mm)	1153	1207
N	48	92

samples with precipitation volume below 8 mm collected at Site 1 was 39 and the precipitation volume was 146.2 mm (10.5% of total volume). These samples were excluded from consideration since the collected volumes did not suffice to perform all the required analyses.

Except for the ammonium at both sites and potassium and nitrates at Site 2, the precipitation weighted average (PWA) concentrations of investigated parameters kept within the ranges found in bulk samples of urban areas (1).

The Kvarner Bay area is affected by seasonal air mass trajectories typical for the southeastern Europe. The trajectory directions are classified into:

- ❑ the long track of maritime air masses from the northwestern Europe, predominantly in winter, that results in long-range transport of atmospheric pollutants;
- ❑ northeasterly continental flow originating in the eastern Europe that is dominant in summer;
- ❑ westerly maritime flow from the Mediterranean, most frequent in autumn and winter and resulting in the highest wet deposition;
- ❑ south-southwesterly flow from north Africa, most frequent in winter and spring, bringing desert air and dust from the Sahara (6).

The lowest rainwater pH values are associated with air mass trajectories from the northwestern Europe. The westerly maritime flow from the Mediterranean is associated with higher rainwater pH values, as well as with the highest precipitation depth and higher wet deposition. The southwesterly air mass trajectories are associated with the Saharan sand episodes, the so called »yellow rains«, with pH value often well above 7.

Previous results of rainwater analyses show that the Kvarner Bay area and the neighbouring mountainous region of Gorski kotar are the most affected by the rain acidity (7). While this is particularly evident in the city of Rijeka, the sea salt and/or soil dust partially neutralise the rainwater acidity in the neighbouring islands (3). Unfavourable meteorological conditions in the city of Rijeka are responsible for frequent air pollution episodes. The local washout of the atmosphere further contributes to acidification of precipitation (3, 7).

Detailed analysis of rainwater composition at both sites in the city of Rijeka has led to several observations. First, rainwater acidity is higher in the city centre due to the local washout of the atmosphere (8), but also because of the possible partial neutralisation of the rainwater samples by ammonia and soil dust at the suburban site. This fact is emphasized by the comparison of median pH values at both sites. PWA concentrations of hydrogen ions when converted to pH values are 4.52 for Site 1 and 4.74 for Site 2.

Second, PWA concentrations of sulphates are similar at both sites, but the marine contribution to sulphates is estimated to 30% at Site 1 (3).

Third, while PWA concentrations of chlorides are similar at both sites, sodium is almost doubled at the suburban Site 2. Therefore, the sea-salt correction of some parameters studied is doubtful. The Cl/Na ratio of 0.65 is substantially lower than that of the sea water (1.17), which suggests that there is another source of sodium, possibly the soil dust (9).

Fourth, PWA concentration of nitrates is higher at the suburban Site 2. Fertilisers used in the neighbouring gardens are the likely additional source of nitrates. Another

possible source of nitrates is the nearby highway, but we do not have any exact data to prove this fact.

Fifth, higher PWA concentrations of calcium, magnesium, and potassium at Site 2 indicate the effect of soil dust on rainwater composition (1).

Sixth, PWA concentrations of ammonium are almost twice as high at Site 2 as at Site 1, probably due to the use of fertilisers in the nearby gardens. This assumption is supported by the fact that PWA concentrations of ammonium keep within the range of values observed in the areas without intensive agricultural activities in Holland. Furthermore, the $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio (2.96) exceeds the stoichiometry value of 2 and is typical of the areas with a known ammonium source (4).

Differences in PWA concentrations of sulphates, nitrates, and ammonium are reflected in the wet deposits of sulphur and nitrate. The total amount of deposited S- SO_4 is similar at both sites. The sea-salt contribution reaches approximately 30% at Site 1, while the amounts of N- NO_3 and N- NH_4 are almost doubled at the suburban site (Table 2).

Table 2 Total deposition of sulphur and nitrogen (g/m^2) in the period March 1990–May 1991

Parameter	Site 1	Site 2
	City centre (ref. 3)	Suburban area
S- $[\text{SO}_4^{2-}]$	2.00	1.99
S-non sea-salt $[\text{SO}_4^{2-}]$	1.35	
N- $[\text{NO}_3^-]$	0.79	1.30
N- $[\text{NH}_4^+]$	1.27	2.56

CONCLUSION

The detailed analyses of the rainwater content at two sampling sites in the city of Rijeka has led to the following conclusions:

- Higher rainwater acidity in the city centre is due to the local washout of the atmosphere. Furthermore, sea-salt aerosols significantly contributed to the sulphate (31%), calcium (20%), magnesium (85%), and potassium (20%) contents;
- Chemical composition of rainwater collected at the suburban Site 2 is affected by soil dust and/or fertilisers used in the nearby gardens. The consequence is a partial neutralisation of rainwater resulting in a rise in pH values. This is particularly evident when the pH medians at both sites are compared;
- The obtained results stress the importance of appropriate selection of sampling sites for a precipitation chemistry survey.

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Sažetak

KEMIJSKI SASTAV OBORINA S DVIJE MJERNE POSTAJE U RIJECI

Uspoređeni su rezultati analize oborina skupljenih od ožujka 1990. do svibnja 1991. na dvije mjerne postaje u Rijeci. Prva se postaja nalazi u širem središtu grada, na terasi Zavoda za javno zdravstvo, na visini od oko 30 m te stotinjak metara udaljena od mora. Druga je postaja Državnoga hidrometeorološkog zavoda u Rijeci, postavljena na 1,5 m od tla, na livadi u predgrađu, 120 m nad razinom mora. U uzorcima oborina izmjerene su volumno otežane koncentracije vodika, sulfata, nitrata, klorida, amonijaka, natrija, kalija, magnezija i kalcija. Usporedbom dobivenih rezultata nađeno je da je povišena kiselost u središtu grada posljedica lokalnog ispiranja atmosfere. Nadalje, na toj je postaji očit utjecaj morskih aerosola na sadržaj sulfata, kalcija, magnezija i kalija. Analiza oborina s postaje u predgrađu odražava jak utjecaj čestica tla te sredstava koja se rabe pri obradi zemlje u obližnjim vrtovima. Posljedica toga je djelomična neutralizacija oborina s povišenjem vrijednosti pH. Sadržaj istaloženog S-SO₄ podjednak je na obje postaje, dok je sadržaj istaloženog N-NO₃ i N-NH₄ gotovo dvostruko viši na postaji u predgrađu. Dobiveni rezultati upozoravaju na važnost odabira lokacije za praćenje kemijskog sastava oborina.

Ključne riječi:

kemijski sastav oborina, kiselost oborina, mokro taloženje, morski aerosoli, utjecaj grada

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