



Physical and chemical properties of dew and rain water in the Dalmatian coast, Croatia

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Abstract

The possibility to use dew water as a supplementary source of water is evaluated in the Mediterranean Dalmatian coast and islands of Croatia, with emphasis on the dry summer season. Two sites were chosen, an exposed open site on the coast favourable to dew formation (Zadar) and a less favourable site in a cirque of mountains in Komiža (Vis Island). Between July 1, 2003 to October 31, 2006, dew was collected together with standard meteorological data. The mean yearly cumulative yields were 20 mm (Zadar) and 9.3 mm (Komiža). During the dry season (May to October), monthly cumulative dew water yield can represent up to 38% of water collected by rainfall. The chemical properties of dew and rain water were analyzed during three years (2004 – 2006) in Zadar. The mean pH and electrical conductivity (EC) values were comparable for dew and rain water, $pH \approx 7$ and $EC \approx 180 \mu\text{S cm}^{-1}$, corresponding to low mineralization. The dew and rain water are in conformity with the World Health Organization directives for potability, except for Mg^{2+} .

1. Introduction

Dew water is the result of atmospheric vapour condensing on a substrate that has cooled down because of a radiation deficit. When the relative humidity (RH) of ambient air is high enough, typically $RH > 70\%$, radiative cooling can allow the substrate to fall below the dew point temperature and counterbalance the latent heat of condensation. Dew water yield is limited by the available cooling energy, in the order of $25 - 150 \text{ W m}^{-2}$ [1-2] and the yield cannot exceed $\sim 1 \text{ mm day}^{-1}$. In this paper we characterize the chemical properties of dew water versus rainwater

in the Dalmatian area and assess to what extent dew water is potable. A three-year study was carried out from 2004 to 2006 in Zadar (Croatia). The measurement period had 408 dew events (36.3% in 2004, 37.4% in 2005 and 37.9% in 2006 and 312 rain events (34.7% in 2004, 30.8% in 2005 and 20.1% in 2006).

The first measurement site is located at the meteorological station of the Hydrometeorological Institute in Zadar (Croatia), at latitude $44^{\circ}08' \text{ N}$ and longitude $15^{\circ}13' \text{ E}$, 5 m a.s.l., on the Adriatic coast, north of Zadar, on a peninsula at about 10 m from the sea. The direction of the dominant winds during the night is NE. Windspeed is measured at 10 m elevation.

The second site is in Vis Island at Komiža ($43^{\circ}03' \text{ N}$, $16^{\circ}06' \text{ E}$, at 20 m a.s.l.). It is a town and harbour at the foot of the Hum peak (587 m) on the western coast of the island. The city is situated in the centre of a mountainous cirque open to the sea to the SW. The Vis Island is about 140 km away from Zadar. The annual mean rainfall is 817 mm (mean computed between 2003-2005) and very erratic: the annual coefficient of variation is 65%. Because of the situation, this site is representative of a poor location for implementing dew collection; the dew yields will thus be considered as a minimum in the area.

Dew was collected on condensers of $1 \text{ m} \times 1 \text{ m}$ inclined at a 30° angle from horizontal coated with OPUR condensing foil. Dew quantities were collected and its volume V measured daily in the morning, corresponding to water collected by gravity flow in a polyethylene bottle. The remaining dew drops were scraped from the surface. Classical meteo parameters were also recorded. Frost was excluded from the dataset.

The dew and rain samples were sent to the chemical laboratory in Zagreb every two weeks and in the interim the samples were stored in a refrigerator at 3°C . The following determinations

were performed (i) physico-chemical properties: pH, conductivity EC, (ii) chemical concentration; cations: NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , anions: HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- .

2. Dew yields

The dew yield data are shown in Fig. 1 (evolution) and the statistics are summarized in Table 1. Zadar had 408 dew days with a mean cumulative yearly dew yield of about 20 mm. The daily dew yields rarely exceeded 0.4 mm.

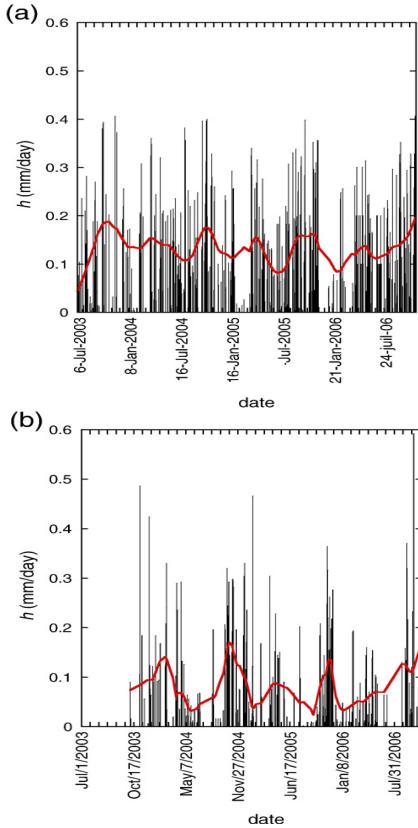


Figure 1 Dew yields h (mm/day) evolution for both experimental sites. The curves correspond to 10% data weighting. (a) : Zadar, (b) : Komiža.

3. Physico-chemical analysis

The statistical and physico-chemical analysis of the elements characteristic of dew and rain water shows that dew and rainwater are of alkaline nature. In both rain and dew water the mean average conductivity is low, $\text{EC} \approx 200 \mu\text{S cm}^{-1}$, corresponding to low total mineralization $\approx 0.77 \text{ mg L}^{-1}$ (dew and rain).

The concentration of the various ions shows that the sum of the cations (Σ cations) is higher than the sum of the anions (Σ anions). Some anions were thus missing in the measurements, in agreement with the fact that the total measured mineralization is in the order of 85 mg L^{-1} , as compared with the above estimation of 150 mg L^{-1} from the conductivity.

Table 1: Various physico-chemical properties of rain water between 2004 and 2006

Dew: 408 events between 2004 and 2006									
	2004			2005			2006		
Measurements	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
pH	6.93	5.69	7.78	6.62	5.45	7.78	6.58	5.53	7.57
EC ($\mu\text{S cm}^{-1}$)	216.48	41	1117	195.66	23	1861	174.31	19	719
Ca^{2+} (mEq L $^{-1}$)	2.11	0.08	9.7	1.79	0.17	7.49	1.25	0.12	6.7
Na^+ (mEq L $^{-1}$)	0.42	0.0087	10.55	0.22	0.025	0.99	0.3	0.03	1.64
Mg^{2+} (mEq L $^{-1}$)	0.35	0.0016	14.52	0.14	0.014	0.56	0.2	0.002	2.66
K^+ (mEq L $^{-1}$)	0.054	0.0019	1.25	0.073	0.004	1.16	0.05	0.004	0.26
NH_4^+ (mEq L $^{-1}$)	0.036	0	0.18	0.017	0	0.026	0.1	0	1.4
H^+ (mEq L $^{-1}$)	0.0002	$<10^4$	0.002	0.0004	$<10^4$	0.0035	0.0004	$<10^4$	0.003
Cl^- (mEq L $^{-1}$)	1.35	0.025	73.8	0.27	0.042	1.22	0.35	0.049	1.6
SO_4^{2-} (mEq L $^{-1}$)	0.11	0	2.34	0.066	0.0091	0.25	0.07	0.013	0.45
NO_3^- (mEq L $^{-1}$)	0.015	0	0.092	0.0093	0	0.062	0.01	0	0.1
HCO_3^- (mEq L $^{-1}$)	0.0065	0.0025	0.31	0.038	0.0014	0.31	0.032	0.001	0.19

Rain: 312 events between 2004 and 2006									
	2004			2005			2006		
Measurements	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
pH	6.37	4.33	7.99	6.5	4.24	8.67	6.13	4.51	7.76
EC ($\mu\text{S cm}^{-1}$)	182.19	5	4850	228.53	6	4980	123.6	9	2211
Na^+ (mEq L $^{-1}$)	0.92	0.009	35.62	1.001	0.004	21.78	0.65	0.025	19.26
Ca^{2+} (mEq L $^{-1}$)	0.52	0.024	4.71	0.83	0	12.09	0.25	0.054	1.52
Mg^{2+} (mEq L $^{-1}$)	0.29	0	11.66	0.4	0.007	7.32	0.27	0.029	4.3
NH_4^+ (mEq L $^{-1}$)	0.027	0	0.58	0.019	0.0001	0.15	0.021	0	0.1
K^+ (mEq L $^{-1}$)	0.026	0.0006	0.8	0.025	0.0007	0.4	0.02	0.002	0.4
H^+ (mEq L $^{-1}$)	0.0028	$<10^4$	0.046	0.0023	0	0.057	0.0028	$<10^4$	0.031
Cl^- (mEq L $^{-1}$)	0.94	0.015	34.86	1.57	0.0054	44.62	0.63	0.025	20.54
SO_4^{2-} (mEq L $^{-1}$)	0.061	0.004	1.36	0.12	0.0013	3.74	0.038	0.0003	0.72
HCO_3^- (mEq L $^{-1}$)	0.05	0.0001	0.5	0.113	0.0001	2.4	0.026	0.0001	0.29
NO_3^- (mEq L $^{-1}$)	0.015	0.0016	0.095	0.013	0.0004	0.12	0.012	0.0007	0.046

3.1. pH

The evolution of pH for both dew and rain is presented in Fig. 2. The dew pH ranges between 6 and 7.5, with a mean value of 6.7 and the rain pH between 5.3 and 7.3, with a mean value of 6.4. The pH of rain is on average slightly more acidic than

the dew pH, by about 0.4 pH units. This difference between dew and rain pH can be attributed to (i) differences in the atmospheric composition of aerosols and gas at high elevation (cloud) and low elevation (dew) [3-4] and (ii) the amount of time where the rain and dew droplets are exposed to the environment [5].

3.2. Electric Conductivity (EC)

The electric conductivity (EC) of dew during the sampling period ranged from $19 \mu\text{S cm}^{-1}$ to $1861 \mu\text{S cm}^{-1}$, with a mean of $204 \mu\text{S cm}^{-1}$ and a standard deviation of $177 \mu\text{S cm}^{-1}$. These values are comparable to the conductivity of rain whose EC values ranged from $6 \mu\text{S cm}^{-1}$ to $4980 \mu\text{S cm}^{-1}$ with a mean EC of $132 \mu\text{S cm}^{-1}$ and a standard deviation of $214 \mu\text{S cm}^{-1}$.

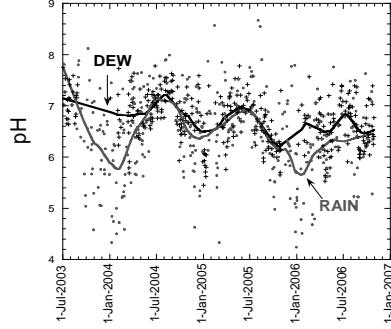


Figure 2: pH evolution for 2004 – 2006 of dew (black crosses and black curve) and rain (gray circles and gray curve). The curves are weighting functions (15% of data).

The mean values are somewhat smaller than the standard value ($400 \mu\text{S cm}^{-1}$ at 20°C) for potable water as requested by the European Commission [6].

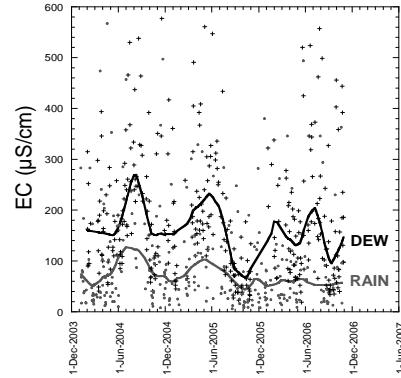


Figure 3: Evolution of dew (black crosses and black curve) and rain (gray circles and gray curve) electric conductivity. The curves are weighting functions (15% of data).

3.3. Ionic concentration

The average ionic concentrations (in mEq L^{-1}) of the major chemical species as obtained from the dew and rainwater analyses for three years are presented in Fig. 4. In dew water, the cations concentrate in different ways:
 years 2004, 2005: $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{NH}_4^+$
 year 2006: $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{NH}_4^+ > \text{K}^+$.
 The concentration of anions follows the same evolution, with $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^-$, except in 2006 where $\text{NO}_3^- > \text{HCO}_3^-$. Concerning rainwater, the concentration of ions is different from what was observed in dew. For cations, one observes:
 year 2004: $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+ > \text{K}^+$
 year 2005: $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{NH}_4^+$
 year 2006: $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+ > \text{NH}_4^+$
 In contrast, the anions evolve/move in the same way throughout the study period, $\text{Cl}^- > \text{SO}_4^- > \text{HCO}_3^- > \text{NO}_3^-$.

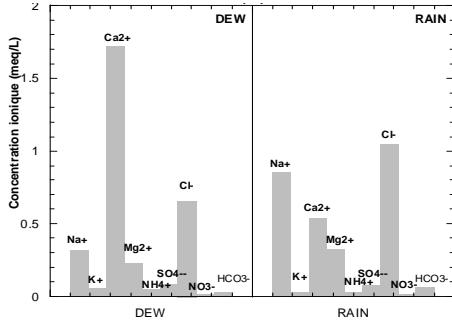


Figure 4: Mean concentration values (mEq L^{-1}) of different ions in dew and rain for 2004–2006

4. Sea contribution

In order to estimate the contribution of the different ions, the sea-salt fraction (SSF) was calculated. The other species are expressed to be as the no sea origin (no sea-salt fraction, NSSF).

The totality of Na^+ considered of sea origin is the principal reference of the calculation as well as the ionic concentration of sea water. The parameters SSF and NSSF are described by:

$$\%(\text{SSF})_X = 100 \times \frac{(\text{Na})(X_{\text{sea}} / \text{Na}_{\text{sea}})}{X} \quad (1)$$

Here X is the dew and rain ion concentration, X_{sea} is the concentration of ion in bulk seawater, and Na_{sea} the concentration of the Na reference ion in bulk seawater. The excess or non sea-salt fraction NSSF_X , is defined as (concentrations in mEq L^{-1}):

$$\%(\text{NSSF})_X = 100 - \%(\text{SSF})_X \quad (2)$$

The results presented in Table 2 show that the ratios $\text{SO}_4^{2-} / \text{Na}^+$, $\text{Ca}^{2+} / \text{Na}^+$, K^+ / Na^+ and $\text{NO}_3^- / \text{Na}^+$ in dew were found to be higher than those in seawater. The large values in dew indicate a contribution from crustal and anthropogenic sources. The high ratios of Ca^{2+} , K^+ , SO_4^{2-} and NO_3^- with Na^+ suggest a non-marine origin of these components. The values of SSF% and NSSF% support this observation. Approximately 99% of Ca^{2+} , 88% of K^+ , 84% of SO_4^{2-} and 99% of NO_3^- in dew samples originate from non-marine sources. Mg^{2+} concentration in dew water is generally affected by both dust and sea-salt particles in the atmosphere, as well as the Cl^- ions ($\% \text{SSF} = 54\%$). In contrast, in rainwater the high NSSF of Ca^{2+} and NO_3^- indicates that they are not influenced by the sea, whereas the other ions show a strong sea

contribution. The high contribution of Cl^- (95%) especially corresponds to sea-salt particles in the atmosphere (Table 2).

Table 2: Comparison of the ratio $\%(\text{SSF})_X$ and $\%(\text{NSSF})_X$ for dew, rain and sea water

Ions	Sea water ratio	Dew ratio	Rain ratio	Dew %SSF	Dew %NSSF	Rain %SSF	Rain %NSSF
$\text{Ca}^{2+} (\text{mEq L}^{-1})$	0.044	5.548	0.616	0.793	99.206	7.1396	92.860
$\text{Mg}^{2+} (\text{mEq L}^{-1})$	0.227	0.741	0.372	30.595	69.404	61.006	38.994
$\text{K}^+ (\text{mEq L}^{-1})$	0.022	0.190	0.0279	11.559	88.440	78.833	21.167
$\text{Cl}^- (\text{mEq L}^{-1})$	1.166	2.129	1.220	54.766	45.233	95.501	4.499
$\text{SO}_4^{2-} (\text{mEq L}^{-1})$	0.040	0.264	0.084	15.121	84.878	47.123	52.877
$\text{NO}_3^- (\text{mEq L}^{-1})$	0.00002	0.035	0.015	0.056	99.943	0.132	99.868

5. Conclusion

In the Mediterranean Dalmatian area, both dew and rain water generally meet the WHO requirements for potable water (except for Mg^{2+}). Passive dew harvesting could thus serve as a useful complementary source of water when other sources are lacking. The two sites investigated here provide an overview of the range of dew water production that can be obtained from an unfavorable site (Komiža, 9.3 mm/y) and a more favorable one (Zadar, 20 mm/y). In the summer dry season (May – October), the monthly contribution of dew water compared to rainfall is on order of 38% (July 2004) and has reached 120% (summers 2003 and 2006). Refurbishing abandoned traditional rain collectors (impluviums), which are numerous in the Dalmatian area, would be a viable option to collect rain and dew water.

References

- [1]. Garratt, J.R., Segal, M. On the contribution of atmospheric moisture to dew formation. *Boundary-Layer Meteorol* 45, 209–236, 1988
- [2]. Nikolayev, V., Beysens, D., Gioda, A., Milimouk, I., Katiushin, E., Morel, J.P. Water recovery from dew. *J. Hydrology* 182, 19–35, 1996
- [3]. Wagner, G., Steele, K., Peden, M. Dew and frost chemistry at a midcontinental site, United States. *J. Geophys. Res.* 97, 20591–20597, 1992
- [4]. Jiries, A. Chemical composition of dew in Amman. *Atmospheric Research* 37, 261–268, 2001
- [5]. Beysens, D., Ohayon, C. Muselli, M., Clus, O. Chemical and biological characteristics of dew and rain water in an urban coastal area (Bordeaux, France). *Atm. Environment* 40, 3710–3723, 2006
- [6]. Rodier, J. *L'analyse de L'eau: Eaux Naturelles, Eaux Résiduaires, Eau de Mer.* 8^e édition. Dunod, Paris. 1365p, 1996