

Variation of pH and concentration of nutrients and minerals during rain-events

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1. Introduction

Detailed information concerning the actual ‘forest damages’ in Europe is needed, specifically regarding the main processes on atmospheric immission on forest ecosystems. In recent years, investigations on the composition of rainwater have been based on monthly, weekly or daily sampling periods (Verry, 1983; Klöti, 1989; Mosello, 1996). To reduce the effects of evaporation and chemical reactions in the samples left in the field for long periods, sampling on an event base has become increasingly common (Radojevic, 1995a; Khare, 1996; Kennedy, 1979).

In the published reports, a large variation in concentration of nutrients and minerals in precipitation during rain-events is established, usually with a peak of concentration at the beginning of an event. Data from sequential precipitation samplers give us more information to evaluate the deposition rate (flux and concentration) on an event basis. An Australian investigation showed that the most influential factors on the deposition rate were the season and the wind direction (Crockford, 1996). It is mentioned in Khare (1996), that during monsoon showers in India, 50 % of the total concentration of the ionic components is washed out in the first 7.2 mm of rain, based on 5 events in 1994. On a process level it is distinguished between the mechanisms transferring material to cloud droplets before they begin their descent as a raindrop (rainout) and those processes transferring material to falling raindrops (washout). It is maintained that washout is the dominant process in the early part of an event, while rainout seems to determine the composition of the rain in the latter part of an event.

This information in Khare (1996) does not explain the processes which are responsible for the variation in concentration during rain-events. As the particles in precipitation are composed of aerosols and gases in the atmosphere, they were fixed by raindrops or icecrystals during cloud condensation (rainout) or scavenged during rain-events (washout). Their chemical composition has also been reported in Fowler (1980), Prokop (1996) and Baechmann (1996).

The concentration of nutrients and minerals in the precipitation is an essential factor effecting the biochemical processes at these locations. Not only the load but also the concentration of minerals and nutrients in wet deposition can be decisive in ecosystem processes. Recently, near real-time pH measurement within several rainstorms have been applied, using a continuous flow system (Jennings, 1992; Radojevic, 1995b; Tyree, 1981). The H⁺ ion is a dominating element in wet deposition. Peaks in H⁺-concentration can affect several parts of a natural ecosystems like canopy (Schreiber, 1996), soilwater and root system, groundwater, lakes and aquatic wildlife.

2. Experimental and methods

This study is based on the following assumptions:

- (i) Scavenging processes during rain-events are responsible for peaks in concentration of minerals and nutrients at the beginning of rain-events (washout), followed by decreasing concentrations in the latter part of the rain-events (rainout).
- (ii) A maximum of acid particles in the atmosphere will be washed out at the beginning of a rain-event, leading to peaks in H^+ -concentration and low pH-values, followed by increasing pH-values in the latter part of the rain-events (rainout).

The investigation area is situated in the Alptal-valley, a rural region in the Swiss prealps with yearly precipitation amounts up to 2300 mm. Urban centres in western direction (Schwyz, Zug, Luzern) are delimited by the mountain-ranges Mythen, Rigi and Rossberg (Burch, 1994). Rainwater samples (table 1/) were collected at the climate-station on 1220 m.a.s.l since 1973. Fischer-Riedmann (1995) calculated the nitrogen deposition at this climate station to be $16.3 \text{ kg (N) ha}^{-1} \text{ yr.}^{-1}$ on average in 1993, including an measured quota of 19% for dry deposition.

TABLE 1: Equipment for wet-deposition measurements in the Alptal-valley (Canton of Schwyz)

Pos.	Equipment	Sampling-interval	from	to
1	bulk-deposition	weekly	6. 1973	9. 1996
2	only-wet deposition (DEP)	weekly	12. 1988	9. 1996
3	sequential-precipitation-sampler (SPS)	5 mm / 10 mm precipitation	10. 1989	6. 1993
4	pH-Ombrometer (near real-time)	10 min.	10. 1989	6. 1993
5	pH-analysis in the laboratory	weekly	6. 1990	9. 1996

2.1 Sequential precipitation sampler

To obtain accurate data concerning the variation of the concentration in the wet deposition, a new sampling-apparatus that splits up the precipitation into sequential samples was developed. This automatic ‘only-wet’ sequential precipitation sampler (SPS) was used from October 1989 to July 1993.

This SPS measured up to 6 rain-events during the usual maintenance interval of one week. A new rain-event started after a dry period of at least 24 hours. During every rain-event, the first sample consisted of 5 mm; all other samples consisted of 10 mm of precipitation. To check the sampling device and the laboratory values, the load and the concentration of the weekly samples (DEP), from the ‘only-wet’ double bucket collector (WMO, 1994), were compared with the average concentration calculated from the sequential samples (SPS). The heated inlet funnel allowed to measure snow-events also in winter. In summer, the cooling system for the open rainwater-samples was not adequate to hold the water temperature at the proposed 4°C during hot periods.

In the laboratory, the samples were filtered ($0.45 \mu\text{m}$) and analysed by the following methods: ICP-MS (Inductively coupled plasma - mass spectrometry) for element concentrations like Ca, K, Mg, Na, Si, Al, Ni, P, S and Pb; IC (Ion chromatography) for ions like NO_3 , SO_4 , PO_4 , CL and FIA (Flow injected analyse) for NH_4 .

2.2 Automatic measuring of the pH within rain-events by ombrometer

Near to the sequential precipitation sampler (SPS), an automatic near real-time pH-ombrometer was installed to measure the acidity of the rainfall in intervals of 10 minutes during rain-events. The pH electrode was calibrated biweekly with buffer solution at pH 4 and pH 7. As the ombrometer was gauged in regular intervals, the established precision is estimated at about 0.1 pH units.

3. Results and discussion

3.1 Variation of rain chemistry during rain-events

From 1989 to 1993, 685 samples have been collected during 230 rain-events. The first 76 events have been analysed in detail (18% thunderstorms in summer, 38% summer rain-events, 44% snow-events). Strong variations in concentration during rain-events have been measured in the sequential samples (SPS). Comparing this data with the weekly samples (DEP), the highest and the lowest concentration were found in the sequential samples (SPS). A report on the evaluation of the complete data-set and a detailed description of the instrumentation has been prepared by Waldner (1996).

A typical pattern during short thunderstorms is the high concentrations of nutrients (NO_3^- , NH_4^+) and minerals (Ca^+) at the beginning of a rain-event, followed by a rapid decrease of the concentrations (Fig. 3.1). The reason is the strong initial washout of the atmosphere by raindrops.

In summer rain-events, during which SO_4^- -concentrations exceeding 2 mg/l, the same pattern as in thunderstorms, but at a lower level of concentration, can be recognised. This occurs during stable atmospheric conditions and at low wind velocities. When the SO_4^- -concentration is below 2 mg/l, the concentration of other nutrients and minerals can increase during longer rain-events in combination with heavy winds (Figure 3.1). These winds can bring new nutrient and mineral from the surrounding area to supply the on-going precipitation processes.

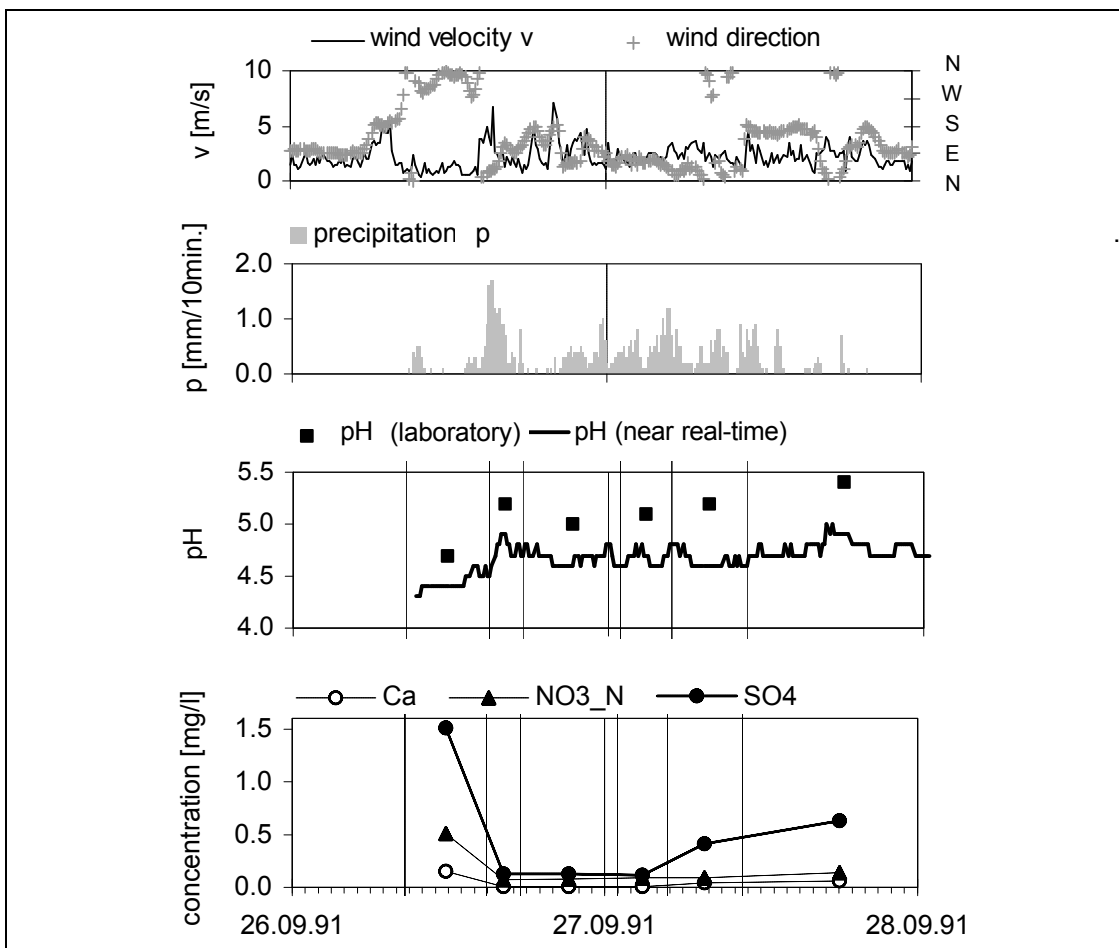


Fig. 3.1: Variation of concentrations (NO_3^- -N, Ca^+ , SO_4^-) and pH during the summer rain-event of 26/27 September 1991. During this rain-event, the sum of precipitation reached 64 mm with a maximum rainfall-intensity of 1.7 mm/10 min.

During snow-events, the concentration of minerals and nutrients in the snow-precipitation was mostly increasing or constant, independent of the SO_4^- -concentration. The reason could be the permanent scavenging of wind-influenced immissions during snow-events. The total load of the wet deposition is higher in winter than in summer. However, the peaks in the concentration of minerals and nutrients are several times smaller in winter than in summer rain-events. Higher element concentration of snow compared to that of rainfall samples are explained by more efficient below-cloud scavenging of atmospheric constituents, especially aerosol particles, by snowflakes (Grosch, 1989).

During the rain events changes in concentration of minerals and nutrients showed generally the same trend in all investigated rain-events. Looking at some concentration ratios in wet deposition, other behaviour was recognised such as increasing Ca^+ -content at the same time when the SO_4^- -concentrations are decreasing. Normally, the concentrations of minerals and nutrients during rain-events were inversely related to the pH.

This pattern can change, if events with high Ca^+ -concentrations occur after periods with low air-humidity and dry winds from the south. Such a typical rain-event was the scavenging of Saharan dust on 23 march 1990 (Schwikowski, 1995), where initial pH-values of 5.9 were observed in the Alptal-valley, followed by pH values down to 5.2 in the next rainout of 39 mm in 10 hours (Waldner, 1996).

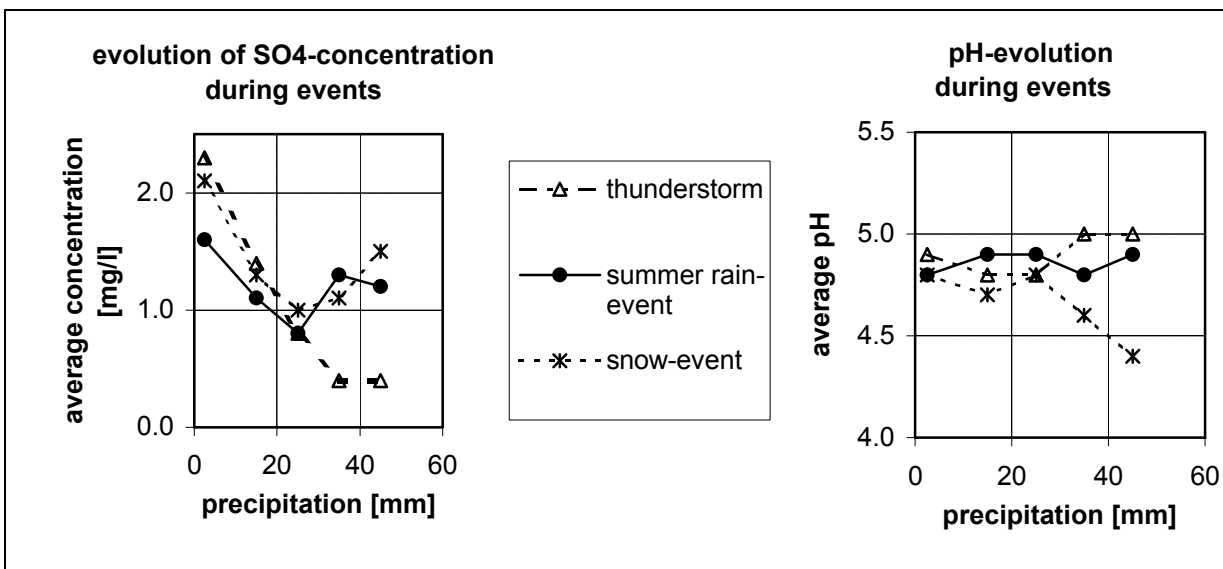


Fig. 3.2: Comparison of the wet-deposition within the 3 types of rain-events (thunderstorm, summer rain-events and snow-events), using all 230 measured events. The average evolution of the SO_4^- -concentration (left) and the pH-evolution (right) during events are shown for the first 45 mm of precipitation.

Figure 3.1 confirms the proposed assumptions, that a maximum of acid particles is washed out at the beginning of a rain-event, followed by lower concentrations at the end of an event, leading to low pH values at the beginning of an event. The hypothesis of the increase of the pH-value in the rain after the initial peak was confirmed only during thunderstorms, but not during snow-events. Based on a full analysis of the 230 events between 1989 and 1993, it was found that 28% of the total content of nutrients and minerals is washed out in the first 5 mm rain of thunderstorms. The corresponding data for snow-events and summer rain-events are 20 % and 13%, respectively (Waldner, 1996).

3.2 Variation of pH during rain-events

The pH, near real-time measured with the pH-ombrometer, showed a range between 3.8 and 6.7 with a weighted mean value of 4.75 in the Alptal-valley. The highest pH value (6.7) was observed during a short Saharan dust event (3.9 mm rain in 6 hours) of 9 march 1990 with a mean Ca^+ -concentration of 4.3 mg/l. Analyses of all the precipitation samples in the laboratory one to 7 days later showed that these pH values were usually higher than the ombrometer data (Fig. 3.3). This shows the difficulties to determine the true value of the pH in precipitation, if the collected samples are not analysed on pH value during the event.

The pH of precipitation water depends on the atmospheric processes like washout and rainout. It is a result of adapted natural components like CaCO_3 from soil erosion and the acid value of gaseous (g) anthropogenic emissions like NO_x (g) and SO_x (g). The concentration of SO_x (g) is not strongly correlated to the resulting pH or the concentration of SO_4^- in precipitation water. On one hand, the SO_4^- indicates an input of gaseous SO_x (g) which leads to an acid reaction in precipitation water. On the other hand, if the SO_4^- originates from the chemical decomposition of salts like CaSO_4 , it does not indicate an acid input (Waldner, 1996).

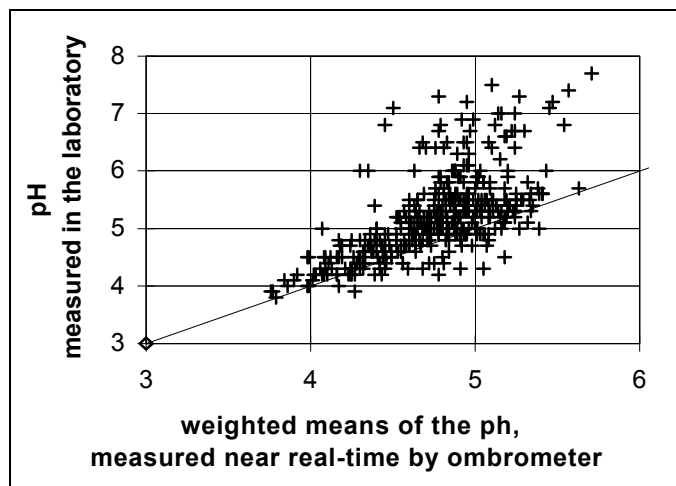


Fig. 3.3: pH-values in precipitation in the Alptal-valley from 1989 to 1993. Comparison of the pH in the sequential samples analysed in the laboratory are shown against the mean, weighted by the sum of precipitation, of the single pH-values of the automatic pH-ombrometer during the corresponding sampling-period. (Unfortunately, the corresponding pH from the laboratory is missing for the highest pH (6.7) measured by ombrometer).

4. Conclusions

During the initial washout of rain-events, the proposed peaks in concentration of minerals and nutrients were verified. But during the final rainout, the proposed decrease of concentrations was confirmed only for thunderstorms and summer rain-events with a large initial impact of SO_4 . The maximum specific deposition rate was observed during snow-events, followed by summer rain-events and thunderstorms.

A maximum of acid particles were scavenged by washout processes at the beginning of rain-events, leading to low pH values in the rain. After this early acid peak, the proposed increase of the pH-values during rainout processes was only observed in thunderstorms. A different pattern shown by rain-events having an impact of Saharan dust, leading to high pH-values in the early washout, followed by decreasing pH in the final rainout. The pH, measured near real-time by the ombrometer, showed a range between 3.8 and 6.7 and was usually lower than the pH in the collected rain-samples.

During thunderstorms in the Alptal-valley, 28% of the total load of elements and nutrients was washed out in the first 5 mm of a rain-event. The corresponding data for snow-events and summer rain-events were 20% and 13%, respectively. Based on the fact, that increasing rainfall intensity generates increasing concentration of nutrients and minerals during rain-events, the 28% washout in the first 5 mm rain in the Alptal-valley are in agreement with the 50% washout in the first 7.2 mm rain during more intensive monsoon showers in India, as reported by Khare (1996).

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