

# Seasonality of the Na/Cl ratio in precipitation and implications of canopy leaching in validating chemical analyses of throughfall samples

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## ABSTRACT

The temporal variation of the Na/Cl ratio in bulk precipitation and throughfall samples was analysed using an extensive data set based on measurements over several years at 11 sites of the Swiss Long-Term Forest Ecosystem Research Programme (LWF). This analysis was prompted by the results of the application of the criteria recommended for validating chemical analyses of precipitation samples in the Integrated Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests). One of these criteria involves verifying that the sodium to chloride (Na/Cl) ratio of the analysed sample is within a restricted range, assuming that most of the chloride originates from sea-spray, and that the contribution of marine ions in atmospheric deposition is in the same molar ratio (0.86) as in sea-water. The range of possible Na/Cl values was defined between 0.5 and 1.5 by ICP Forests in order to account for other possible sources of Na<sup>+</sup> and Cl<sup>-</sup> (natural or anthropogenic). When all sites were considered, approx. 85% of our Na/Cl values were within the proposed range, both for bulk precipitation and throughfall samples. In some cases, low Na<sup>+</sup> or Cl<sup>-</sup> concentrations close to the detection limit were responsible for the Na/Cl ratios outside the range of acceptance. Plotting the Na/Cl ratio versus time revealed a seasonal pattern, which was clearer in the throughfall than in the bulk precipitation samples. This could also account for Na/Cl values higher or lower than the defined limits. The seasonality of the Na/Cl ratio and its components (Na<sup>+</sup> and Cl<sup>-</sup> fluxes) was tested using a regression model. For throughfall, the seasonal pattern of Na/Cl could be ascribed to the seasonally driven canopy leaching of Na<sup>+</sup> and Cl<sup>-</sup>, the intensity of which depended on the tree species.

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## 1. Introduction

High quality measurements of atmospheric deposition are required in several areas of ecological research such as studies of air quality, water quality or ecosystems. Total atmospheric deposition includes a remarkable amount of dry deposition, especially in forests. Dry deposition can be measured by the inferential method, the micrometeorological

method (Wesely and Hicks, 2000), or the throughfall method. While the first two methods require highly sophisticated equipment, the latter relies on relatively simple measurements but implies assumptions about the exchange of ions in the canopy. In particular, negligible uptake and leaching are assumed for sodium (Na<sup>+</sup>) and chloride (Cl<sup>-</sup>).

In Europe, the atmospheric deposition of nutrients and pollutants in forests is one of the key issues addressed by the Integrated Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests), which aims at a better understanding of how

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**Table 1**

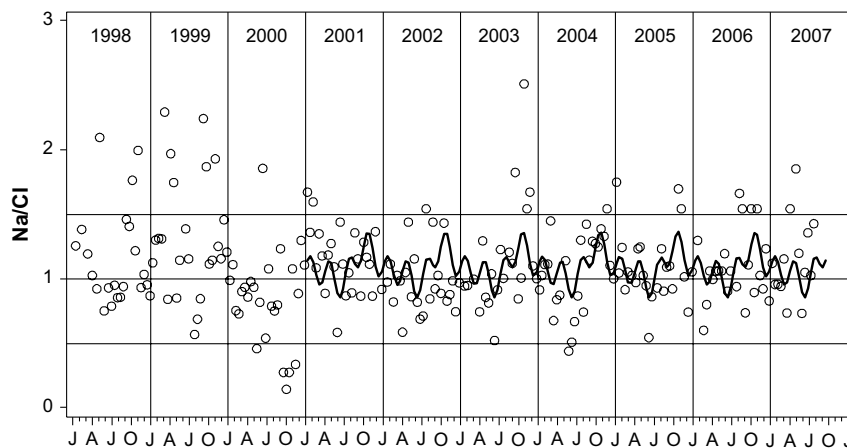
Site characteristics. Mean annual precipitation amounts were derived from precipitation maps established for the period 1961–1990 (FOWG, 2000). Snow cover after Witmer (1986).

Region	Longitude	Latitude	Altitude a.s.l. (m)	Aspect	Mean slope (%)	Annual precipitation (mm)	Number of days with snow cover	Main tree species
<i>Jura</i>								
Bettlachstock	07°25'E	47°14'N	1149	S	66	1549	120	<i>Fagus sylvatica</i> L.
<i>Central Plateau</i>								
Jussy	06°17'E	46°14'N	501	flat	3	977	25	<i>Quercus robur</i> L., <i>Carpinus betulus</i> L.
Lausanne	06°40'E	46°35'N	807	NE	7	1210	63	<i>Fagus sylvatica</i> L.
Othmarsingen	08°14'E	47°24'N	484	S	27	1123	57	<i>Fagus sylvatica</i> L.
Vordemwald	07°53'E	47°17'N	480	NW	14	1115	51	<i>Abies alba</i> Mill.
<i>Lower Alps</i>								
Schänis	09°04'E	47°10'N	733	W	60	1801	97	<i>Fagus sylvatica</i> L.
Beatenberg	07°46'E	46°43'N	1511	SW	33	1305	133	<i>Picea abies</i> (L.) H.Karst.
<i>Alps</i>								
Celerina	09°53'E	46°30'N	1871	NE	34	1024	172	<i>Pinus cembra</i> L.
National Park	10°14'E	46°40'N	1899	S	11	1048	189	<i>Pinus mugo</i> Turra
Visp	07°52'E	46°18'N	695	N	80	689	55	<i>Pinus sylvestris</i> L.
<i>Southern Alps</i>								
Novaggio	08°50'E	46°01'N	950	S	68	2017	48	<i>Quercus cerris</i> L.

natural and anthropogenic stresses affect forest ecosystems in the long term (de Vries et al., 2003). Atmospheric deposition is currently measured in over 500 ICP Forests plots across Europe using the throughfall method. This method involves the parallel sampling of precipitation below the forest canopy (throughfall) and in an open area near the forest stand, using either continuously open collectors (bulk deposition) or wet-only collectors (wet deposition). Deposition measurements have been carried out for over a decade now, but quality control has always been done at the national level. It was only a few years ago that the problem of the quality and thus the comparability of the chemical analyses was addressed at the European level. For this purpose, a working group on quality assurance and quality control (QA/QC) was created within the Expert Panel on Deposition (Mosello et al., 2005). This Expert Panel, which is part of ICP Forests, includes national experts from all participating countries. It ensures the development and harmonization of the monitoring methods and contributes to data evaluations in the field of atmospheric deposition.

The Working Group on QA/QC has made (and is still making) an important contribution to the improvement of the overall quality of the measurements by addressing quality aspects not only in the field and the laboratory (e.g. evaluation of the analytical methods) but also in the validation of results. In the validation stage, four consistency checks on chemical data are currently recommended (Mosello et al., 2005): 1) the ion balance, 2) a comparison between measured and calculated conductivities, 3) a comparison between the sum of the inorganic forms of nitrogen and the total nitrogen, and 4) the Na/Cl ratio. In this paper we focus on the Na/Cl ratio.

In areas close to the sea, sea salt is a major contributor to sodium and chloride deposition, and the molar Na/Cl ratio in precipitation is typically that of sea salt, namely 0.86 (Keene et al., 1986). However, the calculation of the Na/Cl ratio has also proved useful in sites far from the sea. The ICP Forests Manual proposed a range between 0.5 and 1.5 (molar values) as being acceptable (Ulrich et al., 2006). Samples with a Na/Cl ratio outside this range should be re-analyzed. However, if the second run of analyses confirms



**Fig. 1.** Temporal variation of the molar Na/Cl ratio in bulk precipitation (dots) at Jussy, and regression curve (bold line) calculated with data after 01.01.2001 ( $\text{Na/Cl} = 1.098 + 0.05 \cos t - 0.1 \sin t - 0.06 \cos 2t + 0.113 \sin 4t$ ;  $R^2 = 0.17$ ,  $P < 0.0001$ ).

**Table 2**

Variability of the Na/Cl ratio with concentrations (c) close to the determination limit (L). The uncertainty  $\Delta$  of a measured concentration is defined as  $\Delta = \max(L, 0.10 c)$ . Example with  $c_{\text{Na}} = 2 L_{\text{Na}}$  and  $\text{Na/Cl} = 1$ .

	Concentration, c [mg L <sup>-1</sup> ]	Determination limit, L [mg L <sup>-1</sup> ]	Uncertainty, $\Delta$ [mg L <sup>-1</sup> ]	Lower limit, c - $\Delta$ [mg L <sup>-1</sup> ]	Upper limit, c + $\Delta$ [mg L <sup>-1</sup> ]	Concentration, c [ $\mu\text{eq L}^{-1}$ ]	Lower concentration, c - $\Delta$ [ $\mu\text{eq L}^{-1}$ ]	Upper concentration, c + $\Delta$ [ $\mu\text{eq L}^{-1}$ ]
Na <sup>+</sup>	0.16	0.08	0.08	0.08	0.24	6.96	3.48	10.43
Cl <sup>-</sup>	0.25	0.01	0.025	0.225	0.275	7.04	6.34	7.75
Na/Cl						Ratio 1.0	Lower ratio <sup>a</sup> 0.4	Upper ratio <sup>b</sup> 1.6

<sup>a</sup> The lower Na/Cl ratio is calculated as the ratio between the lower Na<sup>+</sup> concentration and the upper Cl<sup>-</sup> concentration.

<sup>b</sup> The upper Na/Cl ratio is calculated as the ratio between the upper Na<sup>+</sup> concentration and the lower Cl<sup>-</sup> concentration.

the concentrations obtained initially, the analyses may then be validated even when the thresholds are exceeded.

The validation procedures recommended by the ICP Forests Manual have been routinely applied for some years in the deposition monitoring activities of the Swiss Long-Term Forest Ecosystem Research programme (LWF; Cherubini and Innes, 2000; Thimonier et al., 2001). However, the occurrence of repeated deviations from the acceptable range under certain conditions, especially in throughfall samples, led us to assess the applicability of the Na/Cl ratio check more closely.

## 2. Material and methods

### 2.1. Sites

Bulk precipitation and throughfall are currently regularly collected at 11 LWF sites distributed across the five main regions of Switzerland (Table 1; Thimonier et al., 2005). On the Central Plateau, which is the most densely populated region in Switzerland, the deposition levels are moderate. Deposition rates decrease with increasing altitude and are lowest in the Alps. They are highest (up to 35 kg ha<sup>-1</sup> a<sup>-1</sup> for N and 17 kg ha<sup>-1</sup> a<sup>-1</sup> for S in throughfall) in Southern Switzerland, which is subjected to the emissions from the industrialised and densely populated Po Basin (Thimonier et al., 2005). In this paper, we will focus on one site in particular, Jussy, where deviations of Na/Cl from the acceptable range have been most frequent. The site of Jussy is located near Geneva on the Central Plateau. On this site, the forest stand is dominated by oak (*Quercus robur* L. and *Quercus petraea* (Matt.) Liebl.) and hornbeam (*Carpinus betulus* L.). We will also present detailed results

for the site of Celerina, a high-elevation site in the Alps, with Swiss stone pine (*Pinus cembra* L.) as the main tree species.

### 2.2. Sampling procedures

A detailed description of the sampling procedures is given in Thimonier et al. (2005). Bulk precipitation was collected with three funnel-type polyethylene collectors (100 cm<sup>2</sup> opening). In winter at the sites where abundant snowfall can be expected (Bettlachstock, Beatenberg, Schänis, Celerina, National Park, Lausanne and Novaggio), the funnel-type collectors were replaced by a single bucket-type snow collector (30 cm diameter).

Throughfall was sampled with 16 funnel-type collectors of the same design as the collectors used in the open area. The collectors were systematically distributed over two 43 × 43 m subplots. In winter at the sites where abundant snowfall was expected (see above), the 16 funnel-type collectors were replaced by four bucket-type collectors.

The collecting samplers were collected once every two weeks (four weeks at Celerina and Bettlachstock in the winter), and replaced by new ones. All samples were sent by post or brought directly to the WSL Research Institute at Birmensdorf, which coordinates the monitoring activities and evaluates the data. Within 3 days of arrival, the samples were filtered (0.45  $\mu\text{m}$ ) and the conductivity and the pH were measured in the laboratory. All samples were prepared in duplicate, one for the chemical analyses of the macro-elements by the WSL central laboratory, the other for storage at +2 °C to allow for repetition of the analyses should the validation checks reveal inconsistencies.

**Table 3**

Seasonal variation of Na/Cl in bulk precipitation at 11 LWF sites, sorted according to the geographic region. The R<sup>2</sup> values are the coefficients of determination of the regression models for the seasonality. The unweighted median Na/Cl ratio, the lower quartile (P25) and the upper quartile (P75) are reported for each site.

Region	Site	n	Median	P25	P75	R <sup>2</sup>	P	Peaks
Jura	Bettlachstock	126	1.03	0.88	1.29	0.12	P < 0.001	Summer
Central Plateau	Jussy	158	1.05	0.90	1.25	0.17	P < 0.0001	Autumn
	Lausanne	158	1.14	0.99	1.39	0.10	P < 0.01	Summer
	Othmarsingen	165	1.06	0.91	1.23	0.02	n.s.	
	Vordemwald	166	1.04	0.89	1.19	0.02	n.s.	
	Beatenberg	162	1.18	0.96	1.41	0.13	P < 0.0001	Summer
Lower Alps	Schänis	163	1.14	0.99	1.54	0.14	P < 0.0001	Summer
	Celerina	118	0.95	0.72	1.18	0.17	P < 0.0001	Late summer
Alps	National Park	157	0.88	0.73	1.13	0.20	P < 0.0001	Late summer
	Visp	120	1.00	0.85	1.23	0.10	P < 0.01	Spring, autumn
	Novaggio	145	1.07	0.90	1.28	0.11	P < 0.01	Lowest in winter

Ammonium (NH<sub>4</sub><sup>+</sup>) was determined colorimetrically through automated flow injection analysis. Calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), potassium (K<sup>+</sup>) and sodium (Na<sup>+</sup>) were determined by inductively coupled plasma–atomic emission spectrometry. Nitrate (NO<sub>3</sub><sup>-</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>) and chloride (Cl<sup>-</sup>) concentrations were analysed by ion chromatography. Determination limits for Na<sup>+</sup> and Cl<sup>-</sup> were 0.08 mg L<sup>-1</sup> and 0.01 mg L<sup>-1</sup>, respectively. Dissolved organic carbon (DOC) and total dissolved nitrogen have been analysed using a TOC-V analyser (Shimadzu, Tokyo, Japan) since May 2001. Dissolved organic nitrogen (DON) was calculated as the difference between total nitrogen and inorganic nitrogen (NH<sub>4</sub><sup>+</sup>-N + NO<sub>3</sub><sup>-</sup>-N). All the analyses were checked against certified standards. International comparison exercises (e.g. Marchetto et al., 2006) confirmed that the analyses carried out by the WSL laboratory were satisfactory for all ions. One exception was total dissolved nitrogen, which tended to be underestimated at high nitrogen concentrations. The ion balance, the conductivity derived from the ionic composition of the samples and the Na/Cl molar ratio, were calculated for each sample as soon as all the chemical analyses were completed.

### 2.3. Data analysis

The seasonality within the data was tested by introducing harmonic terms (sine and cosine) in a stepwise regression of the dependent variable *x* versus time (e.g. Schleppei et al., 2006), in the form:

$$x = c_1 + c_2 \sin t + c_3 \cos t + c_4 \sin 2t + c_5 \cos 2t + c_6 \sin 3t + c_7 \cos 3t + c_8 \sin 4t + c_9 \cos 4t + c_{10} \sin 5t + c_{11} \cos 5t$$

where  $t = 2\pi/365 \cdot$  (day of the year) and *c*<sub>1</sub>–*c*<sub>11</sub> are regression coefficients.

We included sine and cosine terms up to 5*t* in order to best reproduce the systematic narrow peaks clearly visible on the measured data set. Sine and cosine terms with 5*t* correspond to a period of the sinusoidal curve of 365/5 = 73 days, which allows the model to show processes which go up or down within a little more than one month. This makes the analysis sensitive enough to reveal the important features of the annual cycle, but not too sensitive to single irregularities.

When analysing the seasonality of throughfall fluxes, we applied the regression model to the difference between throughfall and bulk precipitation (net throughfall, also called enrichment) rather than directly to the throughfall fluxes. This allowed us to remove the variability due to variations in incident precipitation.

## 3. Results

### 3.1. Bulk precipitation

#### 3.1.1. Seasonal variation of the Na/Cl ratio

Fig. 1 illustrates the temporal variation of the Na/Cl ratio in bulk precipitation at the LWF site of Jussy from 1998 to mid 2007. It shows a wider spread of the values before

**Table 4** Seasonal variation of bulk precipitation volumes and Na<sup>+</sup> and Cl<sup>-</sup> concentrations. Average Na<sup>+</sup> and Cl<sup>-</sup> concentrations are volume weighted. The R<sup>2</sup> values are the coefficients of determination of the regression models for the seasonality.

Region	Precipitation [mm]			Na <sup>+</sup> concentrations [µeq L <sup>-1</sup> ]				Cl <sup>-</sup> concentrations [µeq L <sup>-1</sup> ]					
	<i>n</i>	R <sup>2</sup>	<i>P</i>	Peaks	Mean	s.d.	R <sup>2</sup>	<i>P</i>	Peaks	Mean	s.d.	R <sup>2</sup>	<i>P</i>
Jura													
Bettlachstock	127	0.07	<i>P</i> < 0.05	Spring to autumn	6.8	33.0	0.17	<i>P</i> < 0.0001	Winter	6.3	37.8	0.19	<i>P</i> < 0.0001
Central Plateau													
Jussy	158	0.02	n.s.		8.2	32.9	0.05	<i>P</i> < 0.05	End of winter	7.8	40.9	0.03	<i>P</i> < 0.05
Lausanne	158	0			8.2	41.6	0.14	<i>P</i> < 0.0001	Winter	7.2	42.3	0.16	<i>P</i> < 0.0001
Othmarsingen	164	0.11	<i>P</i> < 0.001	Spring to autumn	7.8	39.8	0.19	<i>P</i> < 0.0001	Winter (summer)	7.4	40.8	0.15	<i>P</i> < 0.0001
Vordermwald	166	0.04	<i>P</i> < 0.05	Spring to autumn	7.8	31.0	0.12	<i>P</i> < 0.001	Winter (summer)	7.6	32.6	0.09	<i>P</i> < 0.01
Lower Alps													
Beatenberg	162	0.28	<i>P</i> < 0.0001	Spring to autumn	5.0	31.7	0.05	<i>P</i> < 0.05	Winter	4.3	34.6	0.06	<i>P</i> < 0.01
Schänis	163	0.16	<i>P</i> < 0.0001	Spring to autumn	7.5	67.1	0.07	<i>P</i> < 0.05	End of winter	6.4	72.2	0.04	<i>P</i> < 0.05
Alps													
Celerina	118	0.17	<i>P</i> < 0.001	Spring to autumn	5.5	21.1	0.10	<i>P</i> < 0.01	End of winter	5.5	22.8	0.21	<i>P</i> < 0.0001
National Park	160	0.07	<i>P</i> < 0.01	Spring to autumn	6.1	29.6	0.08	<i>P</i> < 0.001	Winter	6.4	33.0	0.12	<i>P</i> < 0.0001
Visp	120	0.04	<i>P</i> < 0.05	Spring to autumn	12.3	122.7	0.12	<i>P</i> < 0.01	End of winter	12.7	124.4	0.11	<i>P</i> < 0.01
Southern Alps													
Novaggio	145	0.13	<i>P</i> < 0.001	Spring to autumn	9.9	59.9	0.12	<i>P</i> < 0.001	End of winter	8.9	59.1	0.15	<i>P</i> < 0.0001

2000–2001, with several values above and below the limits of the acceptable range. Before 2001, the Na/Cl criteria was not systematically used in the validation step, and occasional contamination with  $\text{Na}^+$  or  $\text{Cl}^-$  due to inappropriate procedures cannot be excluded.  $\text{Na}^+$  and  $\text{Cl}^-$  contaminations usually occurred independently of each other, as these two elements are analysed with different analytical methods and instruments. Washed polypropylene tubes are used for  $\text{Na}^+$ , and new, unwashed glass chromatography vials for  $\text{Cl}^-$ .

Since 2001, several samples have had a Na/Cl ratio higher than 1.5. A closer look at these samples with extreme ratios revealed that they have low concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$ , including the sample with the highest ratio observed in 2003. For such samples, the calculated ratio is very sensitive to very small deviations in the concentrations. The quality assurance procedure for the chemical analyses in our laboratory are designed to ensure that the uncertainty  $\Delta$  of the measured concentration  $c$  can be described with  $\Delta = \max(L, 0.10c)$ , where  $L$  is the determination limit. Table 2 illustrates with an example how the uncertainty about concentrations close to the determination limit also effects the uncertainty on the Na/Cl ratio: with a measured concentration  $c_{\text{Na}} = 2L_{\text{Na}}$  and  $\text{Na/Cl} \cong 1$ , uncertainties about  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations result in Na/Cl values ranging from 0.4 to 1.6. In such cases it thus seems appropriate to extend the range of acceptable values for the Na/Cl ratio.

In order to remove the influence of possible  $\text{Na}^+$  or  $\text{Cl}^-$  contaminations prior to 2001, we tested the seasonality only in the data collected after January 1st, 2001.

The regression model introducing sine and cosine functions of time resulted in a coefficient of determination

$R^2$  of 0.17, significant at the  $P < 0.0001$  level (Fig. 1, Table 3). Na/Cl in bulk precipitation tended to be higher in the autumn at Jussy.

Seasonal patterns of the Na/Cl ratio in bulk precipitation were also observed at the two high-elevation sites (above 1800 m) in the Alps, at Celerina and the Swiss National Park, with higher Na/Cl ratios being measured in the late summer (Table 3). Lower, but still highly significant coefficients of determination were obtained at mid-elevation sites in the Jura mountains (Bettlachstock) and in the Lower Alps, with higher Na/Cl ratios in the summer. Jussy was the site on the Plateau where  $R^2$  was the highest. There was no seasonality at the sites in Othmarsingen and Vordemwald, which are both below 500 m. The median Na/Cl ratio in bulk precipitation was higher (ranging from 0.88 in the National Park to 1.18 at Beatenberg) than the ratio in seawater on all sites. If all sites were considered, 84% of all Na/Cl values were within the range of acceptance (0.5–1.5).

### 3.1.2. Seasonal variation of Na and Cl concentrations and fluxes

The highest concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  in bulk precipitation were usually measured in winter (Table 4). This was often related to the seasonal variation in precipitation volumes, which tended to be significantly lower in winter than during the rest of the year.

The site of Celerina, where the seasonal variation of Na/Cl was highly significant, was taken as an example representative of the other sites regarding precipitation and concentration patterns. Fig. 2 illustrates the parallel variations of  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations and fluxes on this particular site.

At Celerina, concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  were highest at the end of the winter. At this time of year,  $\text{Cl}^-$

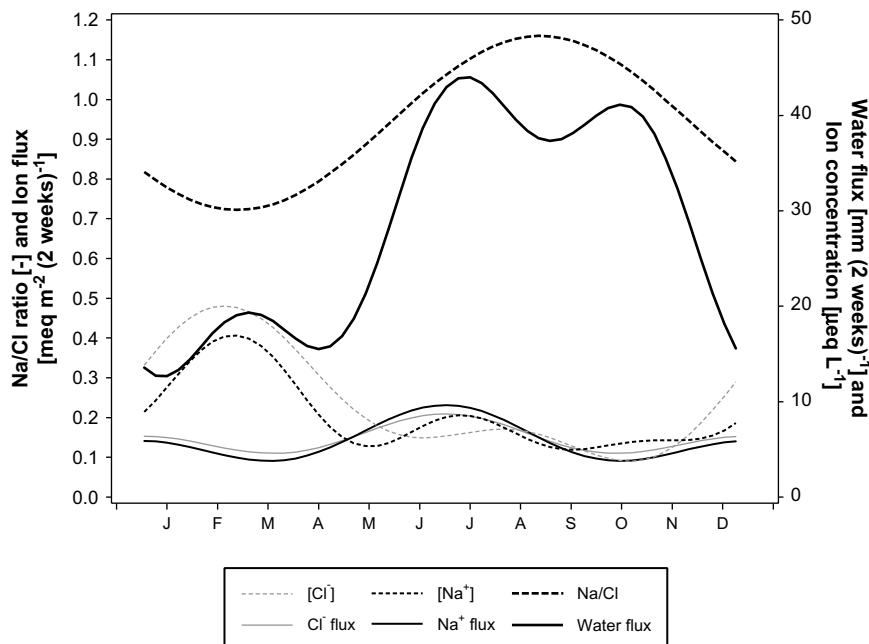
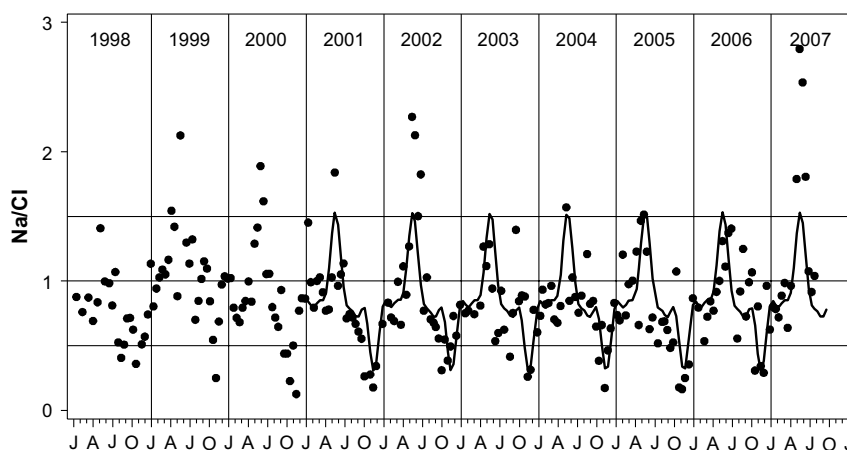


Fig. 2. Modelled seasonal variation of Na/Cl,  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations and fluxes, and bulk precipitation volume at Celerina (concentrations, fluxes and ratio: data after 01/01/2001; precipitation volume: all data since the beginning of the measurements, 13/07/1999).



**Fig. 3.** Temporal variation of the molar Na/Cl ratio in throughfall (dots) at Jussy and regression curve (bold line;  $\text{Na/Cl} = 0.848 - 0.21 \cos t + 0.259 \sin t - 0.07 \sin 2t + 0.136 \cos 3t + 0.144 \sin 3t + 0.059 \cos 5t - 0.06 \sin 5t$ ,  $R^2 = 0.50$ ,  $P < 0.0001$ ).

concentrations exceeded Na concentrations, and Na/Cl was lowest.  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations were lowest in late spring and autumn. During summer and autumn,  $\text{Na}^+$  concentrations tended to be higher than  $\text{Cl}^-$  concentrations, and Na/Cl was highest. The seasonal variation of  $\text{Cl}^-$  concentrations was highly significant ( $R^2 = 0.21$ ,  $P < 0.0001$ ), while the coefficient of determination for  $\text{Na}^+$  concentrations was lower but still significant ( $R^2 = 0.12$ ,  $P < 0.01$ ). The precipitation volume followed a seasonal pattern as well ( $R^2 = 0.17$ ,  $P < 0.001$ ).  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations were highest during the driest period (winter).  $\text{Na}^+$  fluxes ( $R^2 = 0.14$ ,  $P < 0.001$ ) and  $\text{Cl}^-$  fluxes ( $R^2 = 0.09$ ,  $P < 0.01$ ) tended to be highest in the late spring, early summer.

### 3.2. Throughfall

#### 3.2.1. Seasonal variation of the Na/Cl ratio

At Jussy, the seasonal pattern of the Na/Cl ratio in throughfall samples was much more apparent than in bulk precipitation, with lower Na/Cl values in the autumn, and higher values in the spring (Fig. 3). The effects of occasional contamination with  $\text{Na}^+$  or  $\text{Cl}^-$  prior to 01.01.2001 were less clear in the throughfall samples than in the bulk

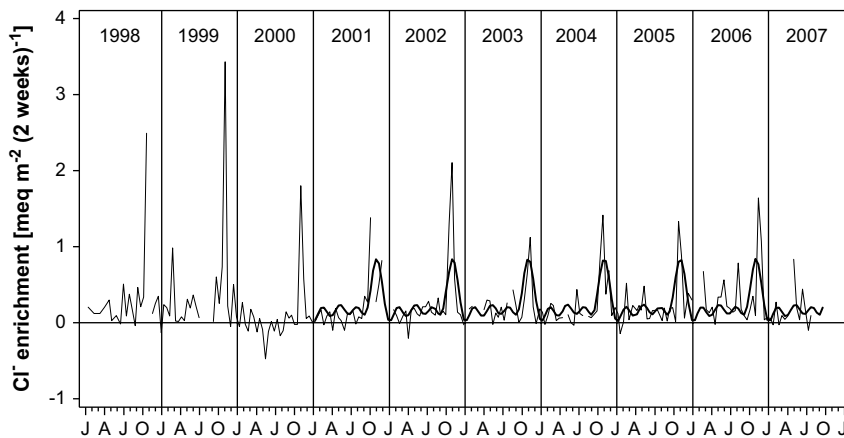
deposition data, because concentrations in throughfall samples were generally higher. However, only data after 01.01.2001 were included in the regression model with sine and cosine functions of time, in order to be in a better position to compare the bulk deposition and throughfall models. The model resulted in a high coefficient of determination, confirming the strong seasonality of the data ( $R^2 = 0.50$ ,  $P < 0.0001$ ).

The site of Jussy is the LWF site where the seasonal pattern of the Na/Cl ratio was clearest and most systematic. Jussy is also one of the sites with the highest proportion (20%) of Na/Cl values outside the range of acceptance. Yet most of these outlier values can be ascribed to the seasonality of the Na/Cl ratio. When all 11 sites were considered, 15% of all Na/Cl values were outside the range of acceptance. At the site level, the proportion of values outside the range varied from 7% (Visp) to 23% (Celerina). Seasonal patterns were detected on all sites (Table 5). The seasonality of Na/Cl in throughfall was highly significant in all broadleaved stands, with peaks either in the spring or in the summer. The seasonality was less marked at coniferous sites except at Beatenberg (*Picea abies* (L.) H.Karst. stand) and Vordemwald (a mixed stand of *Abies alba* Mill., *Picea abies* and *Fagus sylvatica* L.).

**Table 5**

Seasonal variation of Na/Cl in throughfall at 11 LWF sites, sorted according to the vegetation type. The  $R^2$  values are the coefficients of determination of the regression models for the seasonality. The unweighted median Na/Cl ratio, the lower quartile (P25) and the upper quartile (P75) are reported for each site.

Vegetation type	Site	n	Median	P25	P75	$R^2$	P	Peaks
Conifers	Beatenberg	164	0.98	0.80	1.21	0.17	$P < 0.0001$	Summer
	Celerina	120	1.20	0.97	1.42	0.07	$P < 0.05$	Lowest in spring
	National Park	162	1.08	0.89	1.31	0.04	$P < 0.05$	Lowest in spring
	Visp	130	0.89	0.75	1.06	0.10	$P < 0.01$	Spring
	Vordemwald	168	0.74	0.60	0.89	0.10	$P < 0.0001$	Spring
	Broadleaves	Bettlachstock	123	0.88	0.73	1.06	0.19	$P < 0.0001$
Lausanne		163	0.84	0.74	1.03	0.19	$P < 0.0001$	Summer
Othmarsingen		167	0.90	0.79	1.06	0.32	$P < 0.0001$	Late spring, early summer
Schänis		161	0.88	0.73	1.13	0.32	$P < 0.0001$	Spring
Jussy		157	0.80	0.65	1.00	0.36	$P < 0.0001$	Spring (lowest in autumn)
Novaggio		145	1.02	0.84	1.25	0.20	$P < 0.0001$	Summer



**Fig. 4.** Temporal variation of the  $\text{Cl}^-$  enrichment in throughfall ( $E_{\text{Cl}}$ ) at Jussy, calculated as the difference between throughfall and bulk precipitation fluxes for each sampling period. The data are presented as joined lines without symbols. The regression curve ( $E_{\text{Cl}} = 0.25 + 0.072 \cos t - 0.16 \sin t - 0.09 \cos 2t - 0.15 \sin 2t - 0.13 \cos 3t - 0.08 \cos 4t + 0.085 \sin 4t$ ;  $R^2 = 0.39$ ,  $P < 0.0001$ ) is shown as a thicker line.

The mean Na/Cl ratio was lower in throughfall than in bulk precipitation for all sites except the two high elevation sites (Celerina and National Park) (Tables 3 and 5).

### 3.2.2. Seasonal variation of $\text{Na}^+$ and $\text{Cl}^-$ concentrations and fluxes

At Jussy, throughfall enrichment of  $\text{Cl}^-$  showed a sharp peak in the autumn (Fig. 4). The seasonal model resulted in a high coefficient of determination  $R^2$  of 0.39 ( $P < 0.0001$ ).

$\text{Na}^+$  enrichment in throughfall at Jussy also displayed a seasonal variation (Fig. 5), with a pronounced peak in the spring, and a smaller peak in the autumn. Seasonality explained a smaller fraction of variability in the  $\text{Na}^+$  enrichment than in the  $\text{Cl}^-$  enrichment ( $R^2 = 0.31$  and 0.39 for  $\text{Na}^+$  and  $\text{Cl}^-$ , respectively), but its effect was still highly significant. Modelling the throughfall fluxes rather than enrichment resulted in lower coefficients of determination.

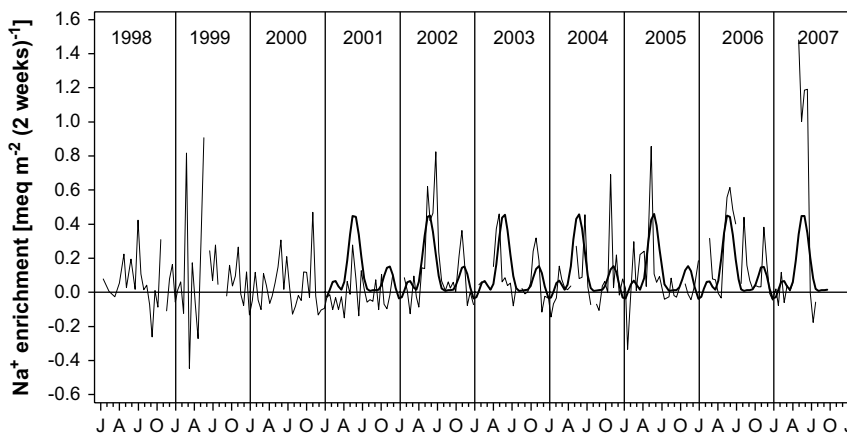
The seasonal variation in  $\text{Na}^+$  and  $\text{Cl}^-$  throughfall enrichment was significant on all sites except Beatenberg (*Picea abies*) (Table 6). The seasonality of  $\text{Cl}^-$  enrichment

was stronger than that of  $\text{Na}^+$ . Peaks of enrichment were mostly observed either in the spring or in the autumn in broadleaved stands, and during the growing season in coniferous stands.

### 3.2.3. Seasonal variation of throughfall fluxes of other nutrients

In order to better understand the processes behind  $\text{Na}^+$  and  $\text{Cl}^-$  enrichment under forest canopies, we assessed the throughfall enrichment patterns for the other nutrients analysed, focusing here again on the sites of Jussy and Celerina.

At Jussy, throughfall enrichment showed a strong seasonality for all nutrients (Table 7). Two main peaks were visible for DOC,  $\text{K}^+$  and  $\text{Mg}^{2+}$  enrichment in the spring and in the autumn (Fig. 6). There was also a clear enrichment peak of  $\text{NH}_4^+$  in the spring. Enrichment of DOC,  $\text{K}^+$  and  $\text{Mg}^{2+}$  was significantly correlated with enrichment of  $\text{Na}^+$  or  $\text{Cl}^-$  (Table 7). Enrichment of inorganic nitrogen ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) tended to be negatively correlated with  $\text{Cl}^-$  enrichment, but there was no correlation between  $\text{NH}_4^+$  and  $\text{Na}^+$



**Fig. 5.** Temporal variation of the  $\text{Na}^+$  enrichment in throughfall ( $E_{\text{Na}}$ , see explanation in Fig. 4) at Jussy and regression curve ( $E_{\text{Na}} = 0.11 - 0.09 \cos t + 0.069 \sin t - 0.13 \sin 2t + 0.062 \sin 3t - 0.06 \cos 4t$ ;  $R^2 = 0.31$ ,  $P < 0.0001$ ).

**Table 6**

Seasonal variation of Na<sup>+</sup> and Cl<sup>-</sup> throughfall enrichment (E<sub>Na</sub> and E<sub>Cl</sub>) at 11 LWF sites, sorted according to the vegetation type. The R<sup>2</sup> values are the coefficients of determination of the regression models for the seasonality.

Site	Species		n	R <sup>2</sup>	P	Peaks
Beatenberg	<i>Picea abies</i>	E <sub>Na</sub>	160	0.02	n.s.	No clear peaks
		E <sub>Cl</sub>	160	0.06	P < 0.01	
Celerina	<i>Pinus cembra</i>	E <sub>Na</sub>	117	0.30	P < 0.0001	Spring (growing season)
		E <sub>Cl</sub>	117	0.31	P < 0.0001	Spring (growing season)
National Park	<i>Pinus mugo</i>	E <sub>Na</sub>	160	0.11	P < 0.0001	Summer (enrichment <0 in winter: road salting?)
		E <sub>Cl</sub>	157	0.24	P < 0.0001	Summer (enrichment <0 in winter: road salting?)
Visp	<i>Pinus sylvestris</i>	E <sub>Na</sub>	119	0.32	P < 0.0001	Growing season
		E <sub>Cl</sub>	118	0.28	P < 0.0001	Growing season
Vordemwald	<i>Abies alba</i>	E <sub>Na</sub>	166	0.11	P < 0.001	Summer (end of winter)
		E <sub>Cl</sub>	167	0.19	P < 0.0001	Summer (end of winter)
Bettlachstock	<i>Fagus sylvatica</i>	E <sub>Na</sub>	125	0.09	P < 0.01	Lowest in summer
		E <sub>Cl</sub>	125	0.34	P < 0.0001	Autumn
Lausanne	<i>Fagus sylvatica</i>	E <sub>Na</sub>	158	0.12	P < 0.001	Spring (autumn)
		E <sub>Cl</sub>	159	0.14	P < 0.001	Spring (autumn)
Othmarsingen	<i>Fagus sylvatica</i>	E <sub>Na</sub>	164	0.17	P < 0.0001	Spring
		E <sub>Cl</sub>	165	0.24	P < 0.0001	Autumn (winter)
Schänis	<i>Fagus sylvatica</i>	E <sub>Na</sub>	161	0.07	P < 0.01	Spring (autumn)
		E <sub>Cl</sub>	162	0.34	P < 0.0001	Autumn
Jussy	<i>Quercus robur</i>	E <sub>Na</sub>	157	0.31	P < 0.0001	Spring (autumn)
		E <sub>Cl</sub>	158	0.39	P < 0.0001	Autumn (spring)
Novaggio	<i>Quercus cerris</i>	E <sub>Na</sub>	142	0.07	P < 0.05	No clear peaks
		E <sub>Cl</sub>	145	0.15	P < 0.0001	Autumn

enrichment even though the modelled NH<sub>4</sub><sup>+</sup> enrichment, like that of Na<sup>+</sup>, peaked in the spring.

At Celerina, the seasonal variation of throughfall enrichment was significant for all elements except Ca<sup>2+</sup> (Fig. 7, Table 8). Peaks of enrichment were less sharp than at Jussy. Enrichment was positive for Na<sup>+</sup>, Cl<sup>-</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, DON and DOC during the growing season. In contrast, enrichment of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> was negative in early summer, indicating uptake of N by the canopy. Negative net throughfall for nitrogen has also been reported at other sites where nitrogen deposition is low (e.g. Lovett and Lindberg, 1993). Na<sup>+</sup> and Cl<sup>-</sup> enrichments tended to peak in the late spring and were strongly correlated with DOC, DON, K<sup>+</sup> and Mg<sup>2+</sup> enrichments (Table 8).

**Table 7**

LWF site at Jussy. Coefficients of determination R<sup>2</sup> for the seasonal regression model applied to throughfall enrichment for each nutrient (data after 01.01.2001), and Spearman coefficients of correlation between Na<sup>+</sup> and Cl<sup>-</sup> enrichment and enrichment for other nutrients (data after 15.05.2001).

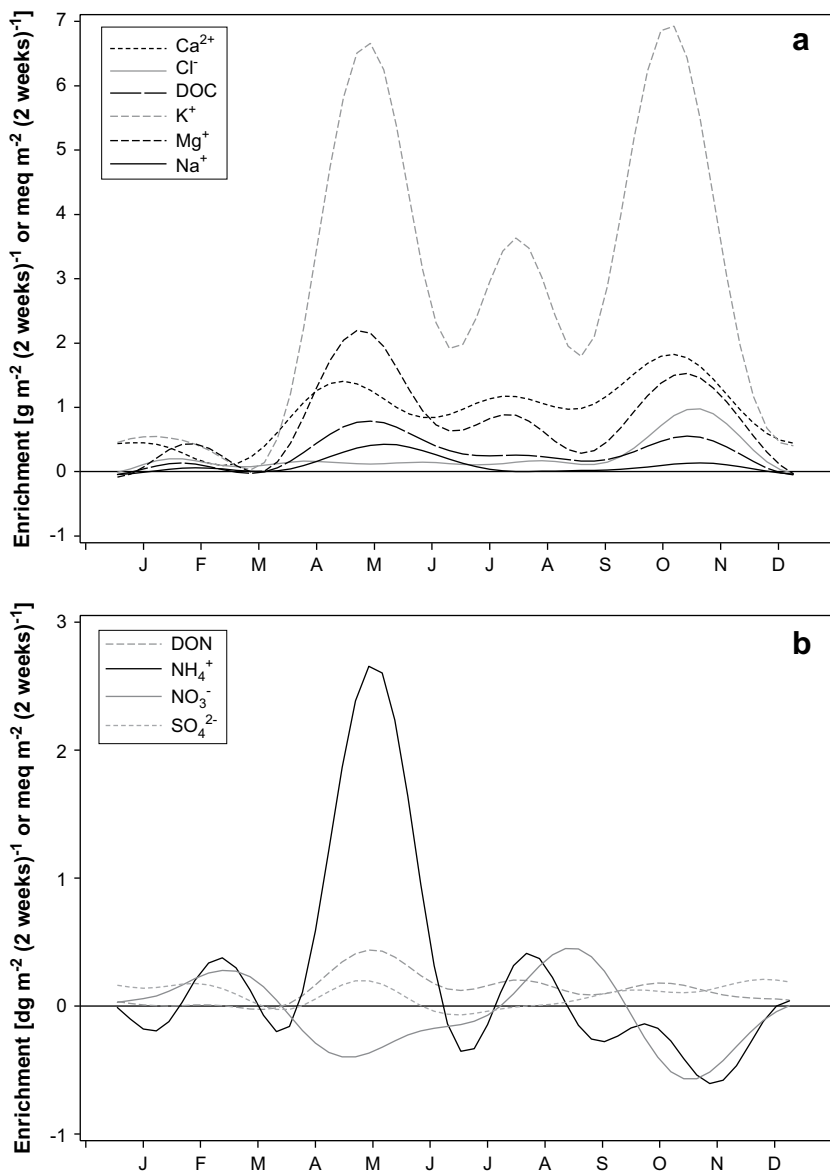
Coefficients R <sup>2</sup> for seasonal model			Spearman coefficients of correlation r with Na <sup>+</sup> and Cl <sup>-</sup> enrichment			
n	R <sup>2</sup>	P	Na <sup>+</sup>	P	Cl <sup>-</sup>	P
K <sup>+</sup>	196	0.46	P < 0.0001	Na <sup>+</sup>	1	
NH <sub>4</sub> <sup>+</sup>	200	0.44	P < 0.0001	Cl <sup>-</sup>	0.55	P < 0.0001
DOC	150	0.39	P < 0.0001	Mg <sup>2+</sup>	0.49	P < 0.0001
Mg <sup>2+</sup>	198	0.38	P < 0.0001	DOC	0.47	P < 0.0001
Cl <sup>-</sup>	197	0.37	P < 0.0001	DON	0.47	P < 0.0001
DON	150	0.37	P < 0.0001	K <sup>+</sup>	0.40	P < 0.0001
Na <sup>+</sup>	196	0.29	P < 0.0001	Ca <sup>2+</sup>	0.37	P < 0.0001
NO <sub>3</sub> <sup>-</sup>	200	0.28	P < 0.0001	SO <sub>4</sub> <sup>2-</sup>	0.32	P < 0.0001
Ca <sup>2+</sup>	198	0.21	P < 0.0001	NH <sub>4</sub> <sup>+</sup>	0.13	n.s.
SO <sub>4</sub> <sup>2-</sup>	200	0.14	P < 0.0001	H <sup>+</sup>	0.11	n.s.
H <sup>+</sup>	200	0	P < 0.05	NO <sub>3</sub> <sup>-</sup>	-0.25	P < 0.01

## 4. Discussion

### 4.1. Bulk precipitation

The Na/Cl ratio in bulk precipitation was substantially higher than the ratio in sea-water at all sites. Similarly, using data from five European countries, Mosello et al. (2005) found higher Na/Cl ratios in precipitation samples of non-marine origin than in samples of marine origin. In their study, precipitation of non-marine origin was defined as having an average Cl<sup>-</sup> concentration <50 µeq L<sup>-1</sup>, which was the case with our samples. The Na/Cl ratio in Switzerland is obviously driven by continental sources of Na<sup>+</sup> such as wind-borne soil dust. This dust, as well as other aerosols or gases containing Na<sup>+</sup> or Cl<sup>-</sup>, can be either dry-deposited (as our collectors are always open) or washed from the atmosphere during rain events and thus wet-deposited.

At some of our sites, Na/Cl followed a significant seasonal variation, with higher ratios in the summer. Shapiro et al. (2007) also observed a strong seasonality in Na/Cl in wet precipitation at West Point, New York, approximately 100 km inland from the Atlantic coast. Unlike our findings, Na/Cl at West Point was lower in the summer and higher in the winter. They found Na/Cl in the winter was close to the sea-water ratio, which they ascribed to the influence of large marine-trajectory storms during colder months. However, Na/Cl strongly decreased in the summer due to regional sources of HCl such as coal combustion, waste incineration or sea-salt dechlorination (a process during which HCl is produced from the interaction of sea-salt aerosols with atmospheric acid gases, such as H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>). At our sites, Na<sup>+</sup> sources seem to predominate over Cl<sup>-</sup> sources. In Switzerland, emissions of HCl peaked in the mid 1980s due to the incineration of increasing volumes of waste (BUWAL, 1995). Since then, the implementation of gas purification



**Fig. 6.** Temporal variation of throughfall enrichment for all elements with a seasonality effect significant at the  $P < 0.001$  level at Jussy.  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  enrichments are in  $\text{meq m}^{-2} (2 \text{ weeks})^{-1}$ , DOC enrichment in  $\text{g m}^{-2} (2 \text{ weeks})^{-1}$ , DON enrichment in  $\text{dg m}^{-2} (2 \text{ weeks})^{-1}$ .

systems in the waste incineration plants has led to a marked decrease in HCl emissions, which are expected to soon reach levels below the levels of the period 1900–1960. At that time, the main source of HCl was coal combustion for industry, household use and rail transport.

The seasonal pattern of Na/Cl in bulk precipitation was most apparent at both sites above 1800 m in the Alps, i.e. in Celerina and the National Park, and, to a lesser extent, at mid-elevation sites (Jura, Lower Alps). One process contributing to the altitude effect is probably the layering of air masses in winter: clear skies in high altitude regions contrast with persistent stratus on the Plateau, which acts like a lid and limits the transport range and deposition of air-borne pollutants. The strong seasonality observed at

Jussy is in contrast with the other low-altitude sites of this study. This might be related to the main wind trajectories at this site (WSW and ENE), which subject Jussy to air masses originating from the Rhone valley. Emissions from the chlorine industry in the Grenoble Basin could thus influence the chemistry of the precipitation at Jussy.

#### 4.2. Throughfall

The Na/Cl ratios in throughfall exhibited a stronger seasonal pattern than in bulk precipitation, especially under broadleaved canopies. We could show that these seasonal fluctuations could be related to enhanced throughfall enrichment of  $\text{Cl}^-$  and  $\text{Na}^+$ , usually in the

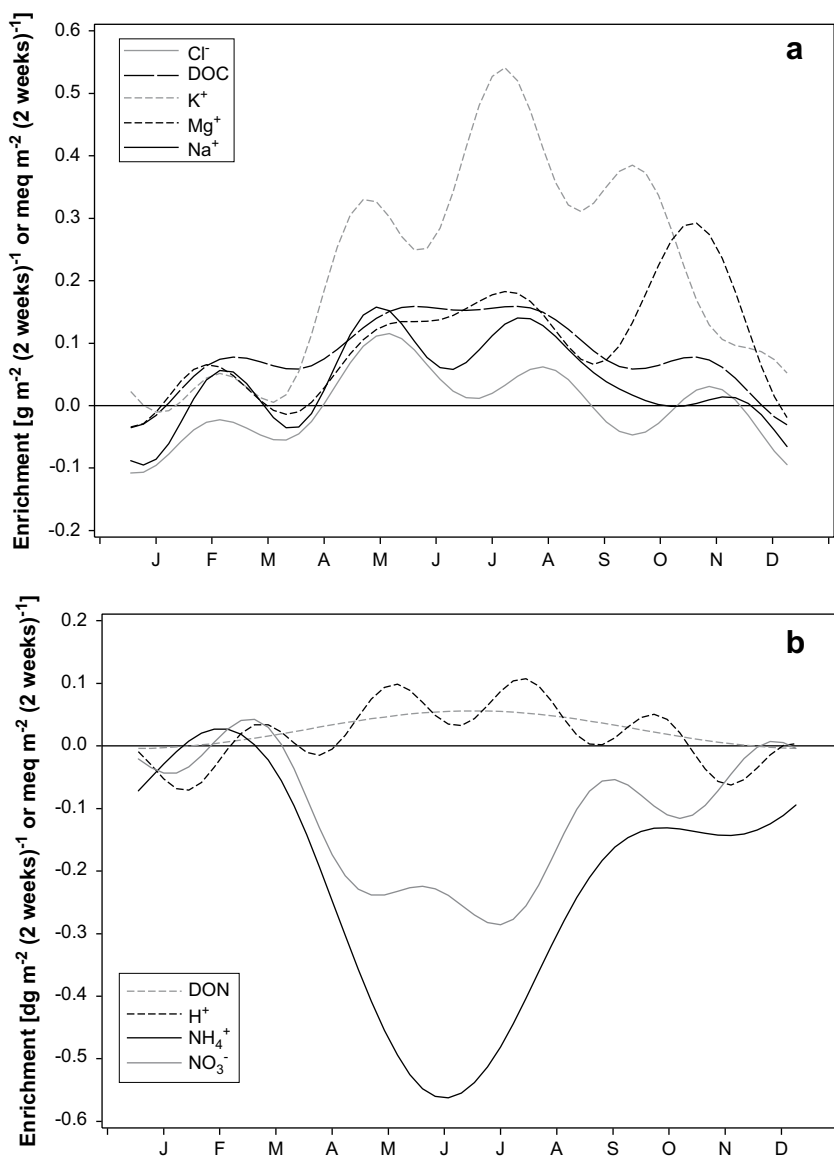


Fig. 7. Temporal variation of throughfall enrichment for all elements with a seasonality effect significant at the  $P < 0.001$  level at Celerina.  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{H}^+$  enrichments are in  $\text{meq m}^{-2} (2 \text{ weeks})^{-1}$ , DOC enrichment in  $\text{g m}^{-2} (2 \text{ weeks})^{-1}$ , DON enrichment in  $\text{dg m}^{-2} (2 \text{ weeks})^{-1}$ .

autumn or spring. Canopy exchange (uptake or leaching) of  $\text{Cl}^-$  is usually considered to be negligible in the models deriving atmospheric deposition from throughfall and bulk precipitation. In these so-called canopy budget models,  $\text{Cl}^-$  enrichment in throughfall is ascribed to the dry deposition of HCl in gas form (e.g. Draaijers and Erisman, 1995). However, the systematically enhanced enrichment in the autumn that we observed in our broadleaved stands over several years of measurements is consistent with the enhanced leaching from senescing plant tissues reported in previous studies (Tukey, 1970). Some other *in situ* studies have also shown that part of  $\text{Cl}^-$  in throughfall can originate from foliage leaching (Neary and Gizyn, 1994; Houle et al., 1999; Moreno et al., 2001; Staelens et al., 2007).

The peak of  $\text{Na}^+$  enrichment in throughfall, which was more pronounced in the spring e.g. at Jussy, is consistent with the observation that  $\text{Na}^+$  can be readily leached from young leaves (in Tukey, 1970). Other authors have found enhanced  $\text{Na}^+$  leaching from emerging leaves (Staelens et al., 2007). Leaching from inflorescences could also contribute to enhanced fluxes in throughfall in May–June.

Patterns of  $\text{Na}^+$  or  $\text{Cl}^-$  enrichments were consistent with the seasonal patterns for DOC, DON,  $\text{K}^+$  and  $\text{Mg}^{2+}$  enrichment, which again supports the claim that leaching occurs from plant tissues (e.g. Parker, 1983; Staelens et al., 2007). At most of our sites, the seasonality of the Na/Cl ratios can thus very likely be ascribed to  $\text{Na}^+$  and  $\text{Cl}^-$  leaching from the canopy, with peaks of leaching occurring at different

**Table 8**

LWF site at Celerina. Coefficients of determination  $R^2$  for the seasonal regression model applied to throughfall enrichment for each nutrient (data after 01.01.2001), and Spearman coefficients of correlation between  $\text{Na}^+$  and  $\text{Cl}^-$  enrichment and enrichment for other nutrients (data after 15.05.2001).

Coefficients $R^2$ for seasonal model			Spearman coefficients of correlation $r$ with $\text{Na}^+$ and $\text{Cl}^-$ enrichment				
$n$	$R^2$	$P$		$\text{Na}^+$	$P$	$\text{Cl}^-$	$p$
$\text{NO}_3^-$	147	0.32	$P < 0.0001$	$\text{Na}^+$	1		
$\text{NH}_4^+$	147	0.30	$P < 0.0001$	$\text{Cl}^-$	0.78	$P < 0.0001$	1
$\text{K}^+$	143	0.26	$P < 0.0001$	DOC	0.72	$P < 0.0001$	0.74 $P < 0.0001$
DOC	115	0.25	$P < 0.0001$	DON	0.70	$P < 0.0001$	0.72 $P < 0.0001$
$\text{Mg}^{2+}$	143	0.25	$P < 0.0001$	$\text{Mg}^{2+}$	0.70	$P < 0.0001$	0.70 $P < 0.0001$
$\text{Na}^+$	142	0.24	$P < 0.0001$	$\text{K}^+$	0.70	$P < 0.0001$	0.67 $P < 0.0001$
DON	114	0.14	$P < 0.0001$	$\text{Ca}^{2+}$	0.57	$P < 0.0001$	0.58 $P < 0.0001$
$\text{H}^+$	147	0.13	$P < 0.001$	$\text{H}^+$	0.40	$P < 0.0001$	0.39 $P < 0.0001$
$\text{Cl}^-$	141	0.11	$P < 0.001$	$\text{SO}_4^{2-}$	0.17	n.s.	0.17 n.s.
$\text{SO}_4^{2-}$	147	0.07	$P < 0.01$	$\text{NO}_3^-$	-0.23	$P < 0.05$	-0.20 $P < 0.05$
$\text{Ca}^{2+}$	143	0	$P < 0.01$	$\text{NH}_4^+$	-0.39	$P < 0.0001$	-0.42 $P < 0.0001$

times of year according to the tree species and the length of the vegetation period, as illustrated by the two examples of Jussy and Celerina. Additionally, insect attacks might also influence throughfall enrichment processes. The peaks of  $\text{NH}_4^+$  observed at Jussy in the late spring could be due to leaching, which Staelens et al. (2007) also observed in a beech stand during leaf emergence. However, these peaks, like the phosphorus peaks (data not shown), could also result from caterpillar outbreaks, which are regularly observed on this site at this time of year. At Beatenberg, where we detected no significant seasonal variation in  $\text{Na}^+$  or  $\text{Cl}^-$  enrichment, the significant seasonality in Na/Cl in throughfall might simply reflect the seasonality of Na/Cl in the incident (bulk) precipitation.

Canopy leaching for  $\text{Na}^+$  and  $\text{Cl}^-$  in the spring and autumn can be estimated, as Staelens et al. (2007) did, by determining the fraction of throughfall enrichment corresponding to dry deposition. The latter can be estimated by calculating a so-called dry deposition factor (DDF), defined as the ratio between throughfall enrichment and bulk precipitation. This DDF is first calculated on an annual scale, excluding periods (spring and autumn) when canopy leaching is believed to occur. Dry deposition of  $\text{Na}^+$  (or  $\text{Cl}^-$ ) in the spring or autumn is then calculated by applying this DDF to the corresponding bulk deposition. Using this approach at the Jussy site, where the seasonality of throughfall enrichment was most marked, we estimated that, on an annual scale, 45% of  $\text{Na}^+$  and 35% of  $\text{Cl}^-$  in throughfall enrichment originated from canopy leaching (median value for the period 2002–2006). The canopy budget models deriving dry deposition from throughfall measurements should then be modified to account for the canopy leaching of  $\text{Na}^+$  and  $\text{Cl}^-$ , as e.g. Staelens et al. (2008) did.

## 5. Conclusion

In this study, we were able to show that leaching of  $\text{Na}^+$  or  $\text{Cl}^-$  from the tree canopy occurred at some forest sites in

the autumn or spring. This leaching shows a distinct seasonality for each site and it influences the Na/Cl ratio. The range of acceptance (0.5–1.5) for this ratio recommended by the ICP Forests manual to validate chemical analyses proved useful as, on average, 85% of our Na/Cl values lay within this range. However, it has to be seasonally adapted for sites with intense  $\text{Na}^+$  or  $\text{Cl}^-$  canopy leaching in the spring or autumn. We recommend as a checking procedure using a plot of the Na/Cl ratio versus time. Furthermore, the occurrence of  $\text{Na}^+$  or  $\text{Cl}^-$  leaching from the canopy belies one of the assumptions of the canopy budget models, which derive dry deposition from throughfall measurements. These models should be adapted to take into account canopy leaching of these ions.

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