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Dry deposition of NaCl aerosols: theory and method for a modified leaf-washing technique

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Abstract

Within the framework of aerosol deposition to vegetation we present a specially designed leaf wash-off method used in a wind-tunnel based study, where leaves of *Quercus robur* L. were exposed to NaCl aerosols. We summarise the principles and illustrate the method for two types of substances, the chloride ion and the sodium ion, and for two levels of aerosol exposure prior to leaf washing. On the average, in the low-exposure experiments (S1), the 1st (2nd) wash-off step provided 90% (96%) of the amount of Cl^- on the leaves. In the high-exposure experiments (S2) the corresponding values were 96% and 99%. For sodium, the general dynamics resembles that of chloride, but the amounts washed off were, in both series, on the average below what would be expected if the equivalent ratio in the tunnel aerosol were to be preserved. Na^+ showed adsorption and/or absorption at the leaf surfaces. The difference between the mean values of the amounts of chloride and of sodium washed off in S1 was not statistically significant, the mean Na^+ to Cl^- difference as a fraction of Cl^- being minus 18%±27%; corresponding values for S2 were minus 16%±9%, however ($p<0.05$). In the latter case, 101±57 µequiv Na^+ per m^2 of leaf area were missing for the equivalent relationship 1:1 with Cl^- to be met. Although uncertainties are thus large, this indicates the magnitude of the Na^+-retention. The method is suitable not only for chloride, an inexpensive and easy-to-handle tracer, but also for sodium under exposure at high aerosol concentrations. Our findings will help design further studies of aerosol/forest interactions.

1 Introduction

Aerosol deposition mechanisms operating in vegetation systems are not well understood. This is because of the wide range of factors such as surface characteristics of aerosol-collecting vegetation elements, aerosol properties, and meteorological conditions. Consequently, several essential aspects of aerosol-ecosystem interactions are associated with high uncertainty, not in the least with respect to nutrient turnover

in forests, and in regard to rates of depletion of the climate-influencing atmospheric aerosol pool. In particular, models of deposition (sink) processes in vegetation (e.g., Slinn, 1982; Wiman and Ågren, 1985; Erisman et al., 1997; Gallagher, 1997; Petroff et al., 2007; Pryor et al., 2008; Fowler et al., 2009) face problems due to the high
5 dependence of deposition rates on leaf characteristics. Aerosols and their biogeo-chemical effects on vegetated canopies have been studied in the field (e.g., Lindberg, 1986) as well as in the laboratory (e.g., Chamberlain, 1967; Ould-Dada, 2001). Among techniques for the study of aerosol deposition onto leaves are net-througfall methods, inferential methods, and leaf-washing techniques (e.g., Draaijers et al., 1996; Wesely
10 and Hicks, 2000; Watanabe et al., 2008). The principles that underpin the wash-off technique have some relationships with those applied in forest biogeochemistry re-search involving precipitation and throughfall measurements; see for instance Lindberg et al. (1986), Lovett and Reiners (1986), Pryor and Barthelmie (2005). Several compli-cations arise in the field when interpreting differences between throughfall and rainfall
15 chemistry in terms of aerosol-borne substances collected by vegetation and "washed off" with precipitation to contribute to throughfall chemistry. However, many of these difficulties can be avoided or minimized in controlled wash-off techniques applied on leaf material exposed to an aerosol in a wind-tunnel environment.

The objective of our contribution is to present theory and methodology details of
20 wash-off techniques that pertain to wind-tunnel studies of aerosol-particle collection efficiencies of oak leaves (*Quercus robur* L.) (Reinap et al., 2009), and that should be applicable to several kinds of vegetation material. We focus on two experimental series, both using a NaCl aerosol that we generated with a modified bubble-bursting technique. One series (S1) consists of nine experimental runs where oak leaves were
25 exposed to relatively low aerosol concentrations, and one (S2) consists of nine exper-imental runs with high aerosol concentrations. We thus illustrate the method for two types of substances – the chloride ion and the sodium ion – that can be expected to in-teract differently with oak-leaf surfaces; Cl^- being essentially inert (e.g., Cappellato and Peters, 1995) and Na^+ exhibiting adsorption and/or absorption (e.g., Ræbild, 1998).

2 Theory and methods

2.1 Leaf/solute dynamics

The mechanisms involved in throughfall studies, and in our procedure for washing off substances deposited on the leaf surfaces after exposing them to an aerosol, can be summarized as follows. The amount $M(\tau)$ of a substance found in the leaf wash-off solute (H$_2$O, in our case) after letting the leaves reside (under slow stirring) a sufficiently long period (τ) of time in the solute is equal to the amount m_{ao} of aerosol deposited on the leaves after exposure to the aerosol-borne substance in the wind-tunnel, plus an amount m_{po} of the substance possibly residing on the leaves' surface prior to the exposure, minus an amount q_{ro} deposited during exposure but possibly retained by the leaves' surfaces and/or absorbed by the leaves, plus an amount $q_{\mathrm{l}\tau}$ possibly leached from the leaves' surface and/or inner fabric. Thus:

$$M(\tau) = m_{\mathrm{ao}} + m_{\mathrm{po}} - q_{\mathrm{r}} + q_{\mathrm{l}} = m_{\mathrm{o}} - q_{\mathrm{ro}} + q_{\mathrm{l}\tau} \tag{1}$$

Assuming first-order reaction dynamics, which holds if the volume of the solute is large enough not to significantly influence reaction parameters, we can thus write, at time t after the start of the washing procedure:

$$dM(t)/dt = k_{\mathrm{a}}[m_{\mathrm{a}}(t) + m_{\mathrm{p}}(t) - q_{\mathrm{ro}}] + k_{\mathrm{l}}q_{\mathrm{l}}(t) = k_{\mathrm{a}}m(t) + k_{\mathrm{l}}ql(t) \tag{2}$$

where $M(t)$ is the amount of the substance (chloride, in our case) in the solute (receptor); $m(t)$ (a donor) originates from aerosol capture $m_{\mathrm{a}}(t)$ during exposure, from amounts $m_{\mathrm{p}}(t)$ possibly residing on the leaves prior to exposure, and from amounts q_{ro} possibly being retained by the leaf surface and thus not wash-off-able; and $q_{\mathrm{l}}(t)$ (also a donor) due to amounts possibly being leached from the leaf; k_{a} and k_{l} are reaction constants.

If the leaf/substance interaction in question has non-leaching characteristics, the term $k_{\mathrm{l}}q_{\mathrm{l}}(t)$ can be neglected. If leaching of the substance does occur, it is likely to be a much slower process than is dissolution of the water-soluble amounts residing on,

and not retained (adsorbed and/or absorbed) by the leaf surface; the term $k_l q_l(t)$ can then be neglected for sufficiently short times (on the scale of minutes) with the leaf in the solute. (On the other hand, for sufficiently long times with the leaf in the solute, $m(t)$ would approach zero and the major contribution to concentration increase in the solute would be $q_l(t)$; a feature that can be exploited in specific studies of leaching characteristics.) Under these conditions, the donor $m(t)$ follows

$$dm(t)/dt = -k_a m(t) \tag{3a}$$

and the receptor

$$dM(t)/dt = k_a m(t) \tag{3b}$$

The solution to this system of differential equations is

$$M(t) = m(0)[1 - \exp(-kt)] \tag{4}$$

with $m(0) = m(t = 0) = m_{ao} + m_{po} - q_{ro}$ as given above.

If the deposited substance is water-soluble and essentially passive at the leaf surface, q_{ro} and $q_{l\tau}$ are both negligible. In our case, the substance used as tracer is chloride, which can be assumed to well meet those conditions (e.g., Cappellato and Peters, 1995; Hansen and Nielsen, 1998; Burkhardt et al., 2001; Rea et al., 2001; Pryor and Barthelmie, 2005). This assumption was also supported by blank tests performed in designing the experimental approach (Reinap et al., 2008). For the chloride case, therefore, $m(0)$ is essentially equal to the amount m_{ao} of aerosol deposited on the leaves after exposure to the aerosol, plus a correction m_{po} for amounts possibly residing on the leaf prior to exposure. If wash-off solutes from the leaves prior to exposure are measured, the upper limit of m_{po} will be known (in our cases close to or below detection limit). (The value of m_{po} would be smaller than the value obtained from the pre-exposure analysis, because the leaves are subject to washing in the pre-exposure analysis step.)

Examples of compounds with considerably more complicated leaf-surface chemistry than that of chloride are heavy metals (often subject to retention by organic surfaces,

so that q_{ro} needs special attention; cf. pioneering studies by Mellor and Maley, 1948; Irving and Williams, 1948) and ammonium, nitrate, potassium, magnesium and calcium (often observed to be leaching from forest canopies, so in such cases q_l needs special attention; cf. Lindberg et al., 1986). Since our chloride tracer was generated from a NaCl solution, opportunities were at hand for studying also the behaviour of Na$^+$. For sodium, adsorption/absorption mechanisms appear to exist and q_{ro} cannot be assumed negligible (cf., e.g., Ræbild, 1998; Marcos et al., 2002; Stachurski et al., 2002); leaching may exist but, if so, should be slow under normal (non-stressed) conditions for deciduous leaves. Comparing the wash-off dynamics of chloride and sodium with the theory approach described above thus offers possibilities for acquiring some insights into the factor q_{ro}. Identification of q_l requires a more elaborate approach, however, with potentially very long wash-off times (on the scale of hours), and is beyond the scope of this contribution.

Clearly, the above equations provide a means for experimental determination of $m(0)$ if concentrations in the wash-off solute can be followed as a function of time, such as through step-by-step measurements. Sequential washing of leaves (or leafed branches) has been used successfully by, for instance, Lindberg and Lovett (1985) and Dambrine (1998). Our technique is to measure $M(t)$ at time points $t=t_1$, $t=t_2$ and $t=t_3$. We note that several mathematical techniques can be used to estimate $m(0)$ from such measurements. For instance, with $t_2=2t_1$ a 2nd order, analytically solvable, algebraic equation is obtained for $x=\exp(-kt_1)$, thus yielding values for $k(=-t_1^{-1}$ $\ln[(M(t_2)-M(t_1))/M(t_1)])$ and $m(0)$ $(=m_{ao}+m_{po}=M(t_1)^2/(2M(t_1)-M(t_2))$. Using $t_3=2t_2$ results in an analytically tractable 3rd order algebraic equation, also leading to estimates of k and $m(0)$; these estimates can be compared with estimates based on t_1 and t_2. Some other choices of t_1, t_2, and t_3 are also helpful.

We tested two alternative strategies with respect to determining M-values. One strategy is to keep (under slow stirring) the leaves in the solute during a time period $t=(0, t_1)$, and then transfer them to a new vessel with the solute and keep them there for a time period $t=(t_1, t_2)$, and so forth, and then add the (declining) amounts measured of

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the substance in the sequence of vessels. Another strategy is to keep the leaves (under slow stirring) in one vessel, and then determining the concentrations (and thus, after the pertinent corrections, the amounts) in sequential samples in the vessel at time points $t=t_1, t=t_2$, et cetera. These two strategies are essentially equivalent, although the first

5　one better emulates the conditions of the solute residing in an infinitely large volume (as assumed by the 1st order reaction dynamics), while the 2nd strategy provides for simpler and faster analytical operations. For the data reported on here, the 2nd strategy was used. There are thus straightforward, although fairly computing-intensive, ways to arrive at estimates of $m(0)$. However, after several tests of various mathematical

10　operations, we found it more efficient to apply standard numerical-library procedures for fitting the 1st-order reaction curve to the wash-off data. Such procedures also have the advantage of providing (through a large number of iterations) curve-fit optimisations, correlation coefficients (r), and uncertainty estimations in terms of standard deviation (s) of the predicted $m(0)$-values.

15　## 2.2　Experimental

Wind tunnels of various types are common in studies of the aerodynamics of, and aerosol deposition to, various vegetative collector arrangements (e.g., Wiman, 1981; Ould-Dada, 2002; Wuyts et al., 2008). Details on the wind tunnel employed in our ex- periments are given in Reinap et al. (2009). The aerosol was generated by a modified

20　bubble-bursting process in a retort outside the tunnel for a Series 1 (giving relatively low aerosol concentrations) and inside the tunnel for a Series 2 (relatively high aerosol concentrations). The retort contained a saturated 36% (by volume) solution of (partly processed) sea salt, whereof $\geq$99.8% is NaCl; a choice made so as to simplify chemical analyses. Although not 100% pure NaCl, aerosol particles generated from solutions of

25　this salt can be expected to show hysteresis effects with respect to aerosol-particle size growth and decline as a function of relative humidity, in contrast to particles generated by oceanic waters with a more complex salt composition. In previous studies, we gen- erated aerosol concentrations lower than in Series 1 and then mostly found negligible

amounts of sodium in the leaf wash-off, whereas chloride could be determined. This general result pointed to sodium to some extent being adsorbed at, and/or absorbed by, the leaves. No leaching was detected. Experiments presented here, therefore, employed moderate and high aerosol concentrations in the wind-tunnel atmosphere.

5   The flow rate of the air jet injected through a nozzle (outlet diameter 1 mm) to "burst" the sea salt solution surface in the retort was controlled with a flowmeter (TSI 6330). Wind speed in the tunnel was controlled through an electronic regulator for the wind generator, and was measured with an air velocity transducer (TSI Model 8455-300). In order to sample aerosol mass an Andersen non-viable 8-stage impactor was used. The
10 multi-stage, multi-orifice cascade impactor operates with a flow rate of 28.3 liters per minute ($L\,min^{-1}$) and with 50% cut-off diameters (µm) from 9 down to 0.43. The complete impactor assembly consists of an inlet cone plus nine stages (eight nozzle plates, eight collection plates, and a backup filter). As backup filter, an 81 mm glass-fiber filter disc was used because of its high collection efficiency for sub-µm particles. The
15 aerosol particles collected by impactor plates and the back-up filters were dissolved in 40 ml 18.2 $M\Omega/cm^2$ Milli-Q^{TM} water in Petri dishes subjected to slow automated shaking for 10 min. Tests showed that only one wash-off step was needed in contrast to the wash-off technique used for oak leaves that require sequential washing as discussed above. The solute was analyzed for Cl^- and Na^+ (accuracy better than 5%) with Ion
20 Selective Electrodes (ISE Orion 9617 and ISE Orion 8611) connected to ISE meter Orion 720 Aplus.

Oak seedlings were cultivated under controlled laboratory conditions under 12 day-light hours at 20 °C. The age of the seedlings may affect morphological leaf properties such as size, shape, firmness and hairiness (Watanabe et al., 2008). In the experi-
25 ments reported here, we used leaves that were on the average 8 weeks old (Series 1) and 24 weeks old (Series 2). On the average, the total single-sided leaf areas of the leaf arrangement (A_{leaf}) were around 0.07 m^2 in Series 1 and 0.04 m^2 in Series 2. A_{leaf} was determined from high-resolution photos of the leaves on the sheet, followed by digital surface-area quantification.

Well-leafed branches were cut from the laboratory seedling bank and washed for 10 min in a vessel containing 400 ml 18.2 MΩ/cm^2 Milli-Q^{TM} water (pre-exposure wash-off step). Branches were then left to dry in a clean-air environment, and then inserted into the wind tunnel in leaf arrangement with the help of a commercially available system (PluggBoxes). At this stage, the aerosol concentration in the wind-tunnel was close to equilibrium (concentration steady-state is typically obtained within less than 0.5 h after system start-up, as found after many preparatory runs preceding the experiments reported here). The arrangement was then exposed to the aerosol for 4 h (a duration found suitable after many test runs preceding the experiments reported here). In Series 1, three runs were performed at 2 ms^{-1}, three at 5 ms^{-1} and three at 10 ms^{-1}. In Series 2, all runs were performed at 2 ms^{-1}. After exposure, the exposed branches were kept under slow automated shaking in a vessel for 20 min, the vessel initially containing 400 ml 18.2 MΩ/cm^2 Milli-Q^{TM} water. After 5, 10 and 20 min, respectively, 30 ml of the solute was taken out for analysis; three sampling steps were thus used. The three post-exposure leaf wash-off solutes were analyzed for Cl$^-$ and Na$^+$ ions with the ISE technique.

2.3 Uncertainty estimations

The uncertainty in $m(0)$ – i.e. $dm(0)$ – is represented by the corresponding s (see Tables 1 and 2) resulting from the curve-fitting procedure. Hence, $dm(0)$ can be calculated at about 5% of $m(0)$. The analytical uncertainty for each impactor stage is <5%, so the total aerosol concentration c as measured by the impactor would be associated with an error <15%, based on the square root of the sum of the squared errors per stage. The uncertainty in time measurement for a 240 min exposure run is less than 1 min, i.e. <0.4%.

3 Results

3.1 The wind tunnel aerosol

The experiments reported here used a salt solution of NaCl with equivalent Na to Cl ratio of 1, for generating the aerosol. We explored whether this ratio was preserved
5 in the wind-tunnel aerosol for the two different series of experiments. Figure 1 shows a strong correlation between Cl^- and Na^+ based on the impactor measurements for the respective Series 1 and 2 (each based on nine experimental runs), and a slope close to 1.

We thus observe an adequate relationship between two elements Na^+ and Cl^- for
10 both series; i.e., equivalent proportions are essentially maintained from the aerosol-generator solution to the wind-tunnel aerosol, and almost perfectly so in Series 2.

We can therefore conclude that the leaf arrangements were exposed to Na^+ and Cl^- in those proportions. If both Na^+ and Cl^- were inert at the leaf surface this proportion would then also be found in wash-off solutes.

15 ### 3.2 Wash-off dynamics

In this section, we present the experimental wash-off data from the first and second series, and the corresponding curve fits. Table 1 gives the resulting values for $m(0)$, r, and s (parameters as defined in the theory framework above) for Series 1. As observed above in Sect. 2, in the final analysis of deposition calculations (cf. Reinap et al., 2009)
20 the value m_{ao} is obtained from the respective $m(0)$-values minus the respective m_{po}-values (which were close to or below detection limit).

Figure 2 illustrates Cl^- and Na^+ wash-off data for Series 1 (leaves exposed to fairly low aerosol concentrations), all nine experimental runs taken into account.

The second series of experiments completes and confirms the general dynamics
25 observed in the data above. Figure 3 illustrates Cl^- and Na^+ wash-off data at $2\,ms^{-1}$ wind speed. Table 2 gives the resulting values for $m(0)$, r, and s.

On the average, in Series 1 the 1st wash-off step provides 90%, and the 2nd step 96%, of the amount of chloride on the leaves. In Series 2 the corresponding values for chloride are 96% and 99%. For sodium, the general dynamics resembles that of chloride, but the amounts washed off are, in both series, on the average below what would be expected if the equivalent ratio in the tunnel aerosol were to be preserved. The difference between the mean values of the amounts of chloride and of sodium washed off in Series 1 is not statistically significant at the 95% confidence level, the mean Na^+ to Cl^- difference as a fraction of Cl^- being minus 18%±27%; corresponding values for Series 2 are minus 16%±9%, however, and thus significant. In the latter case, 101±57 µequiv Na^+ per m^2 of leaf area were missing for the equivalent relationship 1:1 with Cl^- to be met. Although uncertainties are thus large, this indicates the magnitude of the Na^+-retention (parameter q_{ro} for Na^+ as given in Sect. 2).

In order to further detail the different outcomes with respect to sodium in the two series, Fig. 4 shows the relationships in Series 1 between chloride and sodium in terms of equivalents in the wash-offs.

The leaf arrangements were exposed to Na^+ and Cl^- in 1:1 equivalent proportions (see Fig. 1a). However, as Fig. 4 indicates this proportion cannot be identified with statistical confidence in the wash-off solutes from the leaves in the low-exposure Series 1. The number of data is too small to enable assessment of whether retention of Na, or leaching, or a combination of those processes, is involved. In the high-exposure Series 2, however, the relationship between Cl^- and Na^+ in the wash-off solutes (Fig. 5) comes close to the equivalent Cl^-/Na^+ ratio in the aerosol (see Fig. 1b). Since the aerosol in itself contained the Na-to-Cl proportion of the solution from which the aerosol was generated, Fig. 5 thus "fingerprints" the wash-off as emanating to a dominant extent from the artificial aerosol-generator solution, and not from sources of sodium and chloride in the leaves.

It is of interest to explore the combined Series 1 plus Series 2 wash-off data sets. This is done in Fig. 6, which shows that the Series 1 data are essentially contained within the 95% confidence band of the combined set. In addition, although still weak,

the tendency for a deficit of Na^+ in relation to Cl^- in the wash-off emerges more clearly. In analogy, if the combined sequence of data is explored the estimate of the Na^+-retention, in quantitative terms, narrows somewhat, to 59±34 µequiv per m^2 of leaf area (95% confidence).

4 Discussion

Deposits on the leaves depend on concentration in the atmosphere (in our experimental case, the wind-tunnel atmosphere), exposure time, wind speed, leaf morphological characteristics such as leaf age, hairiness, and leaf shape. The primary goal of this paper is to present the principles of the wash-off technique as such, so as to help facilitate further studies of aerosol/forest interactions.

The findings presented above support the usefulness of the method. Chloride is a good and easy-to-handle tracer for exposure studies. However, with some caution exercised, sodium can also be a suitable tracer under exposure at high aerosol concentration. The relationship between Cl^- and Na^+ in equivalents in the aerosol-generator solution is maintained in the aerosol, which confirms the absence of element fractionation in the (modified) bubble-bursting process used. At low aerosol concentrations (around 26 µequiv m^{-3}) and after 4 h of exposure, the Na/Cl ratio in the aerosol could not be identified as preserved in the wash-off solute, and only Cl^- is useful as a tracer. At high aerosol concentrations (around 140 µequiv m^{-3}), however, exposure times of only a few hours are needed and NaCl is a good tracer because we can fairly well recognize our aerosol "fingerprint". The wash-off methodology presented here gives important insights into the wash-off dynamics, for instance, in terms of reaction constants (cf. Sect. 2). Clearly, for NaCl, wash-off durations needed are only around 10–15 min or less.

However, in our experiments we noted that some sodium appears to be missing in the wash-off. Leaf physiology and leaf surface chemistry are among explanatory factors. Because of dynamics and molecular mechanisms of uptake, potassium (K^+),

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as an essential nutrient, and sodium (Na^+) are closely related such that sodium can easily take the place of potassium in the plant cells. This can exert limitations on physiological processes. At high concentrations Na^+ is toxic to most plants. Na^+ toxicity is multifactorial, including osmotic stress, inhibition of vital enzymes and competition with
5   K^+ (Mäser et al., 2002; Ræbild, 1998). Generally, absorption of one ion is reduced as the concentration of another ion is increased in the external medium. For instance, sodium and potassium as well as other ions present will have an inhibitory effect on each other. Thus, sodium ions in our wash-off solutes might be replaced by other ions, such as K^+. Our results regarding Na^+ behaviour towards vegetative surface support
10   the findings by Ræbild (1998).

The morphology and distribution density of epicuticular waxes significantly affect the adhesion of aerosol particles following impaction and interception (Ren et al., 2007). The presence of epicuticular waxes on leaf surfaces often causes water repellence and is highly dependent on type of leaf, season and age of the leaf. Oak (*Q. robur*
15   L.) leaves are covered by waxes and are water repellent when young; however, a few weeks after leaf expansion the waxes are rapidly eroded (Neinhus and Barthlott, 1998). Due to high susceptibility to erosion, waxes easily build an amorphous layer that likely provides a more retentive surface, to which particles adhere, leading to continuously increasing contamination. This holds true not only for fine particles ($<1\mu m$), but also for
20   larger particles, resulting in a comparatively high coverage of the total surface area, up to 8% as reported by Neinhus and Barthlott (1998). Similar findings were reported by Paskova (1989) where *Q. robur* turned out to be one of those species that effectively capture aerosol particles. Furthermore, some experiments studying the retention rate of aerosols to plant surfaces show that this rate can range from less than 10% to over
25   90% of particles captured by the leaf, depending on the species examined. The retention rate appears to be linked to differences in leaf microstructure and orientation in relation to the aerosol flow (Neinhuis and Barthlott, 1997). Such aspects may thus also explain our findings with respect to Na^+ not fully meeting the 1:1 equivalent relationship with Cl^-.

Finally, we observe that there might be possibilities to apply our methodology to other ions than Na^+ and Cl^-, but one must be aware of limitations that can appear as a result of leaf surface characteristics and substance chemical properties. For instance, cations such as K^+, Mg^{2+}, and often also Ca^{2+}, are leached from the foliage (Likens et al., 1977; Lindberg et al., 1989; Ragsdale et al., 1992).

5 Conclusions

Studies of aerosol deposition to plant material are essential to understanding plant-atmosphere interactions and the many related realms of forest biogeochemistry, not in the least within the framework of changes in climate and land use (Reinap et al., 2009). Many problems arising in field studies can be avoided or minimized in controlled wash-off techniques applied on leaf material exposed to an aerosol. In this contribution we have developed and presented details of a technique based on washing leaves after exposure to NaCl aerosols. As expected, the chloride and sodium ions interact differently with oak-leaf surface, inasmuch sodium has a tendency to be adsorbed on leaf surfaces and/or absorbed by leaf tissue. Even though leaf arrangements were exposed to Na^+ and Cl^- in 1:1 equivalent proportions, these proportions were not preserved in wash-offs of leaves exposed to low aerosol concentrations. However, in the high-exposure experiments, the relationship between Cl^- and Na^+ in the wash-off solutes comes close to the equivalent Cl^-/Na^+ ratio in the aerosol. That fingerprints our generated aerosol solution. The method can be applied for Na^+ as tracer if we consider high aerosol concentrations. Our wash-off technique could be used for other ions if one attends to potential complications regarding leaching or retention processes. The use of radioactive substances would help eliminate such problems but, on the other hand, such experimental options would require special (and quite expensive) facilities and working environments. Our approach effectively circumvents such difficulties.

In general, there is a need for more advanced wind tunnel studies under controlled conditions (Reinap et al., 2009; Fowler et al., 2009), not in the least with a focus on

vegetative surface morphology and aerosol composition. The wash-off technique presented here has a high potential for simplifying such investigations and several related challenges with respect to aerosol-deposition modelling, including those that address the influence of forest edges and other heterogeneities on aerosol deposition patterns.

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Table 1. Values for $m(0)$, r, and s pertaining to Fig. 2.

Plot ID	$m(0)$ Cl$^-$ μequiv	r	s	$m(0)$ Na$^+$ μequiv	r	s
1 (2 ms^{-1})	3.40	0.999	0.16	4.42	0.999	0.13
2 (2 ms^{-1})	3.00	0.998	0.20	3.11	0.984	0.71
3 (2 ms^{-1})	4.32	0.999	0.05	5.17	0.999	0.06
1 (5 ms^{-1})	4.83	0.997	0.38	2.43	0.986	0.10
2 (5 ms^{-1})	3.68	0.999	0.06	2.25	1.000	0.01
3 (5 ms^{-1})	3.22	0.995	0.41	3.77	0.999	0.15
1 (10 ms^{-1})	4.64	0.999	0.02	2.40	0.999	0.00
2 (10 ms^{-1})	8.36	0.999	0.18	4.25	0.999	0.09
3 (10 ms^{-1})	6.06	0.999	0.22	3.12	0.999	0.10

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Table 2. Values for $m(0)$, r, and s pertaining to Fig. 3.

Plot ID	$m(0)$ Cl$^-$ µequiv	r	s	$m(0)$ Na$^+$ µequiv	r	s
1 (2 ms^{-1})	29.39	1.000	0.18	22.06	0.998	1.17
2 (2 ms^{-1})	11.61	1.000	0.00	7.01	0.998	0.37
3 (2 ms^{-1})	25.00	0.999	0.90	21.01	0.999	0.47
4 (2 ms^{-1})	17.40	0.999	0.68	14.18	0.998	0.76
5 (2 ms^{-1})	43.80	0.998	2.26	37.79	0.998	2.00
6 (2 ms^{-1})	24.52	0.996	1.79	19.86	0.998	1.07
7 (2 ms^{-1})	18.10	0.997	1.24	16.96	0.996	1.31
8 (2 ms^{-1})	18.81	0.997	1.26	17.60	0.990	1.97
9 (2 ms^{-1})	23.35	0.995	1.99	24.04	0.992	2.43
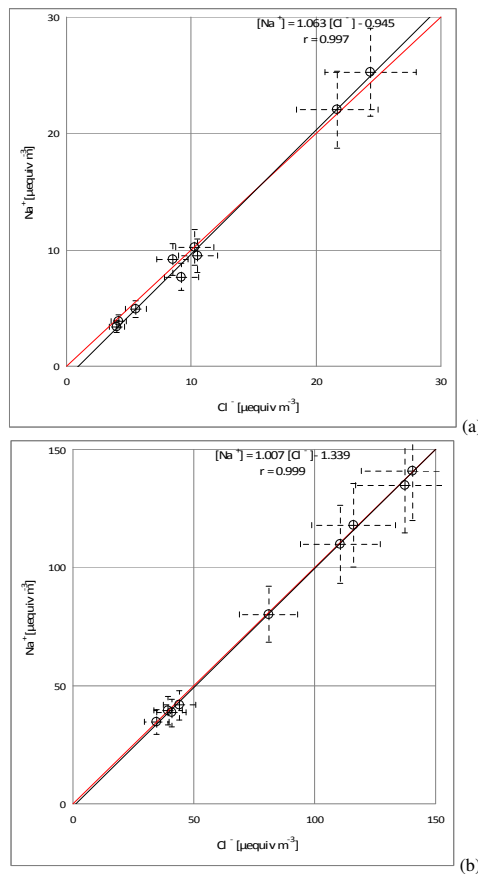
Fig. 1. Relationship between chloride and sodium in terms of concentration (μequiv m^{-3}) based on impactor data from two series of experiments: **(a)** Series 1; **(b)** Series 2. Thin red line indicates the ideal relationship. The respective regression equations are given in each diagram.
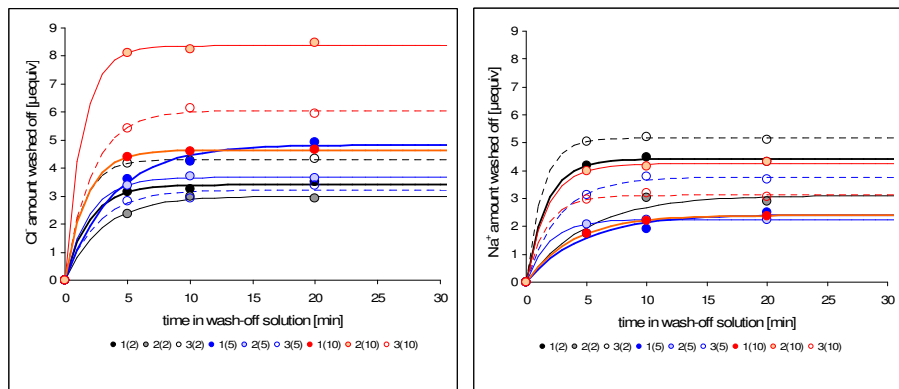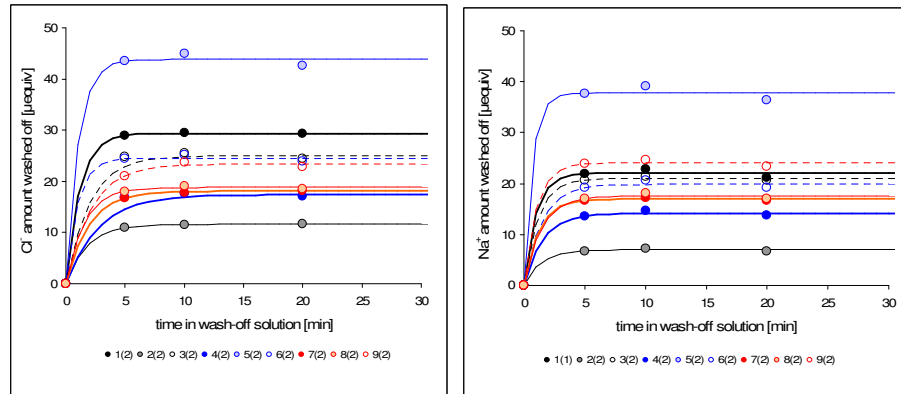
Fig. 2. Measured data from wash-off analyses, and the corresponding theory-based 1st-order reactions curves, Series 1 at low aerosol concentrations. Curves fitted through the use of numerical-library routines. Curve denoted 1(2) refers to run number 1 at $2\,\mathrm{ms^{-1}}$, curve denoted 2(2) refers to run number 2 at $2\,\mathrm{ms^{-1}}$, and so forth, with curve denoted 3(10) thus referring to run number 3 at $10\,\mathrm{ms^{-1}}$.

Fig. 3. Measured data from wash-off analyses, and the corresponding theory-based 1st-order reactions curves, Series 2 at high aerosol concentrations. Curves fitted through the use of numerical-library routines. Curve denoted 1(2) refers to run number 1 at wind speed $2\,\mathrm{ms}^{-1}$ and so forth.
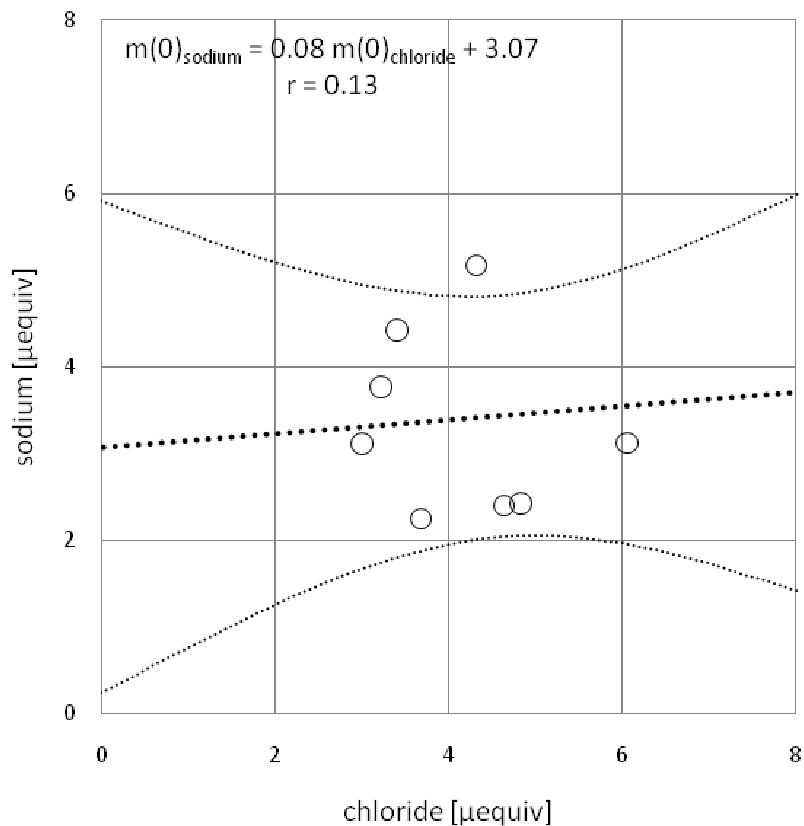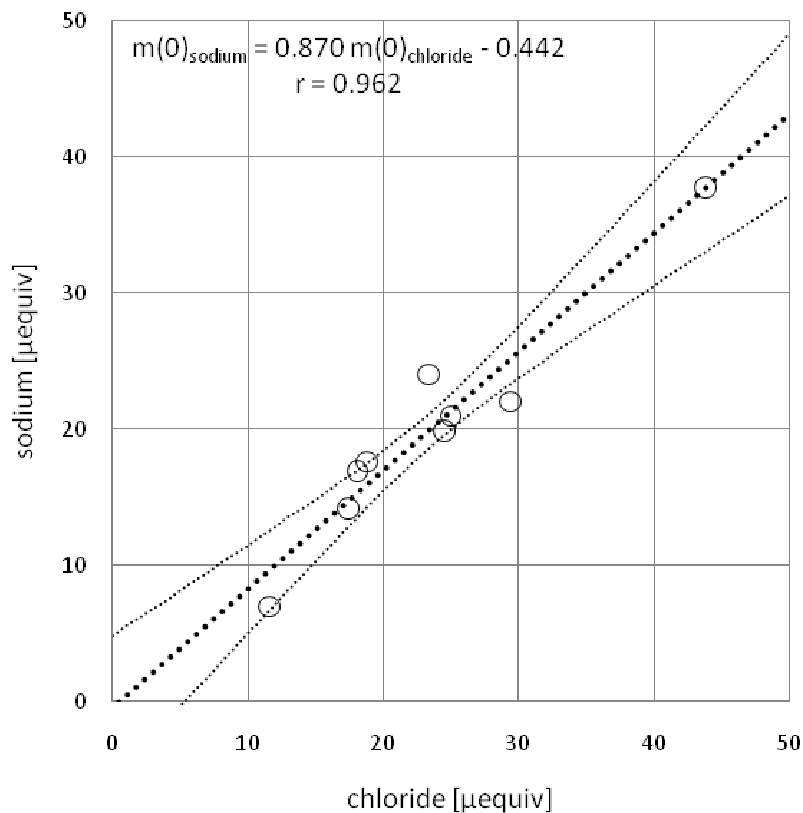
Fig. 4. Relationships between Cl$^-$ and Na$^+$ in terms of equivalents (µequiv), in the wash-offs, for Series 1 (low aerosol concentrations). Unfilled circles: $m(0)$-values calculated from measured data; thick dotted line: linear regression line; area within thin dotted lines is 95% confidence band for the slope of the regression equation. Regression equation and correlation coefficient given in the diagram.

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$$m(0)_{sodium} = 0.870\, m(0)_{chloride} - 0.442$$
$$r = 0.962$$

Fig. 5. Relationships between Cl^- and Na^+ in terms of equivalents (µequiv), in the wash-offs, for Series 2 (high aerosol concentrations). Unfilled circles: $m(0)$-values calculated from measured data; thick dotted line: linear regression line; area within thin dotted lines is 95% confidence band for the slope of the regression equation. Regression equation and correlation coefficient given in the diagram.

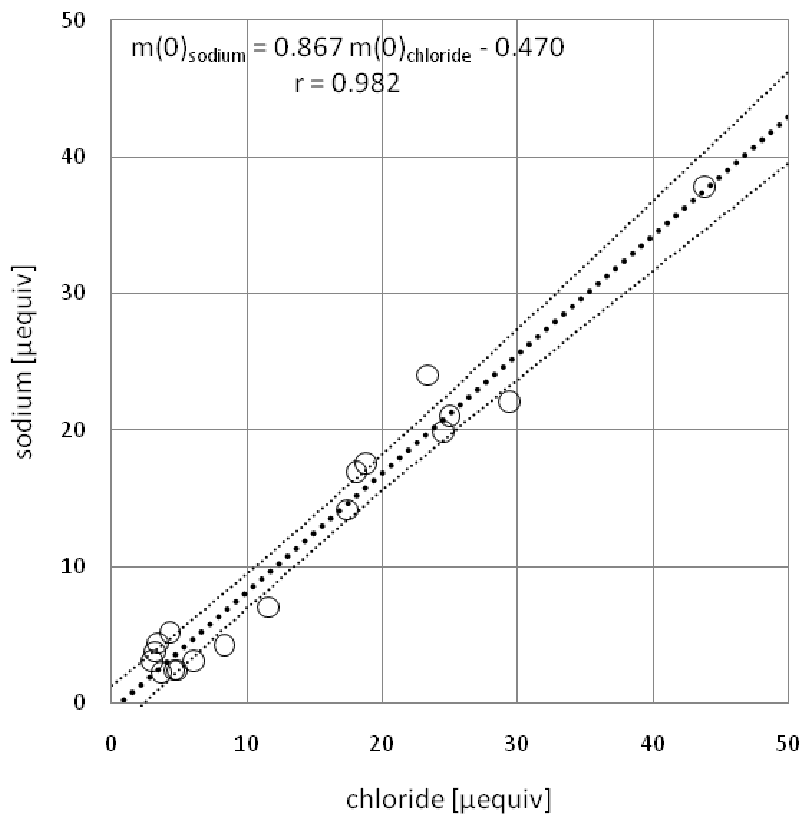$$m(0)_{sodium} = 0.867 \, m(0)_{chloride} - 0.470$$
$$r = 0.982$$

Fig. 6. Relationships between Cl- and Na+ in terms of equivalents (µequiv), in the wash-offs, for the combined Series 1 (low aerosol concentrations) and Series 2 (high aerosol concentrations) data. Unfilled circles: $m(0)$-values calculated from measured data; thick dotted line: linear regression line; area within thin dotted lines is 95% confidence band. Regression equation and correlation coefficient given in the diagram.

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