

Authors' Response to Interactive Comment by Referee #2 (Atmos. Meas. Tech. Discuss., 3, C2302-C2304, 2010) on Reinap, Wiman, Gunnarsson and Svenningsson: "Dry deposition of NaCl aerosols: theory and method for a modified leaf-washing technique" (Atmos- Meas. Tech. Discuss., 3, 3851-3876, 2010)

We thank Referee #2 for the constructive assessment. In particular, we appreciate that the comments to a substantial extent focus on the methodology aspects, since these constitute the essence of our manuscript. Below, we have inserted essential excerpts from the Referee's comments and provided our responses. Figures developed for this response are referred to with letters A and B; figures with Arabic numerals refer to those in our original manuscript.

**Referee comment: The title and introduction of the manuscript suggest a study on dry deposition of NaCl aerosol to vegetation. The main results and the corresponding discussion, however, focus on the wash-off dynamics of sodium and chloride ions from oak leaves. There is no attempt to link these experimental results to the controlling factors of aerosol dry deposition in a wind tunnel experiment or in the atmosphere.**

Authors' response: The introductory part of the manuscript title, and of the manuscript as such, was intended to place the core of the manuscript – i.e., the wash-off methodology *per se* – in a broader context. Elaborating on that context was beyond the scope of our paper. However, reactions to our paper from AMTD Referees suggest that our intentions have led to expectations with respect to the contents of the paper much beyond the scope of this particular contribution. Clearly, a revised version of our paper would better be given the title "Theory and method for a laboratory-based leaf-washing technique for oak leaves exposed to artificially generated NaCl aerosols". In addition, we realize that the introductory part of the manuscript would need to provide a more clear focus on the methodology as such; i.e. on a method that we have identified as important when experimentally assessing the overall question of dry deposition. Alternatively, a much more far-reaching paper could be written, wherein the methodology part would be linked to "the controlling factors of aerosol dry deposition in a wind tunnel experiment or in the atmosphere". That option, however, would lead to a much longer paper.

**Referee comment: The turbulence conditions in the wind tunnel are not characterized, and it is not clear if and how the experimental results can be used under atmospheric conditions. In addition to the reference given for the wind tunnel experiment, some basic information about the setup (e.g. arrangement, size) and the flow conditions (e.g. Reynolds number) would be absolutely necessary in the manuscript.**

Authors' response: Naturally, we agree with the Referee's perception in general. That is, a wide range of wind-tunnel characterizations and experimental conditions could be addressed to enable analysis of aerosol-deposition processes and the extent to which experimental results can be used to improve current understanding of aerosol deposition to "real-world" systems. We feel that the reference given to some of our work (and many references in turn provided in that paper) should be sufficient to help place our wash-off methodology manuscript in that context (which, again, is much broader than the intended focus of our wash-off methodology paper). Again, however, the Referee seems to suggest that a quite different, and much longer paper would be the only option. We do not feel that we can agree with that opinion, because – as the Referee constructively puts emphasis on in the comments

that follow – the issue in focus in our current manuscript is the extent to which an inexpensive and easy-to-handle substance (NaCl) can be used as a tracer to simplify analysis of deposits on leaves exposed to an aerosol. (Several kinds of tracers are of interest, but in the majority of cases they present problems – being expensive, needing quite special logistics, and in some cases posing health threats.) As we note on page 3862, lines 8-10: “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”.

**Referee comment: {In section 2.1, the authors introduce a model of the wash-off dynamics based on first-order kinetics including the amount of aerosol deposited on the leaves during exposure, the amount of aerosol residing on the leaves prior to exposure, and the amount of retained/ absorbed and leached ions.} The explanations in this section [Section 2.1] are hard to follow and should be simplified. In particular, the definitions of the used variables are not consistent (e.g. is  $q_r$  equal to  $q_{ro}$ ? Is  $m_o = m(0)$ ?).**

Authors' response: In order to introduce the methodology in a clear manner it is necessary to be very precise, in terms of mathematics and physics, with respect to processes involved. Our Eq. 1 is needed in throughfall studies in the field, as well as in laboratory approaches, but its implications differ between those two realms. In our case, it defines the situation after a sufficiently long time period ( $\tau$ ) in the solute. Therefore, in our case, where leaves are kept in the solute, that situation is defined by conditions as time  $t \rightarrow \infty$  (not to be mistaken for a “static” situation, which is at hand when analysing throughfall – which does not contain leaves themselves, only a “memory” of the leaves – collected in the field). Therefore, and contrary to what is often found in the literature, it is essential to deepen the theory and explore how that state (defined by  $t \rightarrow \infty$ ) is actually reached. This necessitates Eqs. 2 and 3, which also provide a basis for discussing which terms than can be assumed negligible.

Unfortunately, Eq.1 includes a potentially confusing printing error in the version published online, inasmuch the term  $q_{ro}$  is erroneously given as  $q_r$ , as observed by the Referee. Also, in Eq. 2,  $q_l$  is incorrectly given as  $ql$ ; on line 21 (p. 3854) the term is given in a correct manner. Eqs. 2 and 3 follow standard mathematical notation for differential equations. The parameter  $m_o$  (a constant in Eq. 1) turns out to be identifiable as  $m(0)$  (which is a function of time  $t$  and reaching the value  $m(0)$  at  $t = 0$ ) which in turns out to equate  $M(t)$  as  $t \rightarrow \infty$ .

Except for the mishaps noted above, we cannot see why these equations are difficult to follow. The equations help pin-point details and show how first-order kinetics can emerge in the system. We do not find it easy to provide such detail without invoking mathematical language; but simplifications and ways of better introducing the symbols could be explored.

**Referee comment: It seems that the selected time steps for ion concentration measurements are not adequate for the curve fitting presented in Fig. 2 and 3. For most experiment runs, especially at high aerosol concentrations (Fig. 3), the solute concentration is more or less constant for the three different measurements. The authors themselves acknowledge that 90% (low exposure) and 96 % (high exposure) of the chloride on the leaves is washed off during the first wash-off step. Thus, the model fit is poorly constrained with regard to dynamics, i.e. the reaction constant  $k$ . For example, if additional ion concentration measurements had been made after 2 min, the initial slopes of the presented fit curves might look very different.**

**[Therefore,] I disagree with the author's statement that the "wash-off methodology presented here gives important insights into the wash-off dynamics, for instance, in terms of reaction constants" (p. 3862).**

Authors' response: The averaged wash-off data (cf. Fig. A below) show a behaviour quite typical of a "wash out process". That is, the data underpinning Figs. 2 and 3 in the submitted manuscript correspond to exponential decline of substance amounts at a surface subject to washing; cf. our Eq. 3a. Nevertheless, we naturally agree with the Referee's observation that additional concentration measurements (such as after durations smaller than – or much smaller than – 5 minutes) would have been needed to enable us to follow-up on our statement on page 3862, lines 21-23, that the "wash-off methodology presented here gives important insights into the wash-off dynamics, for instance, in terms of reaction constants (cf. Sect. 2)." However, that statement of ours refers to the methodology as such, and we do not use our data to present a series of reaction constants. Instead, we indicate that potential of the methodology as such, and limit our conclusions to observing that "for NaCl, wash-off durations needed are only around 10-15 min or less" (page 3862, lines 24-25).

Also, although we agree that measurements after durations smaller than 5 minutes would have been desirable, we feel that the Referee might have overlooked the role of the pre-exposure measurements. Those measurements establish an upper limit to the amount of the respective substance (chloride and sodium) in the solute at time  $t = 0$  ( $m_{po}$ , in Eq. 1). In most cases, the pre-exposure wash-off value was below detection limit, and the pre-exposure measurement in itself leads to further wash-off of substances possibly residing at the leaf surfaces before exposure (so that the actual  $m_{po}$ -value should be essentially negligible). This means that values for  $M(t=0)$  were in practice available, and were well approximated by  $M(0)=0$  (as shown in Figs. 2 and 3). Hence, our data sets are better constrained than the Referee suggests. Also, for each sequence and substance, data can be normalised to  $M(20)$ -values, and all data ( $9 \times 4$ ) can then be used to explore the behaviour of  $M(t)$ . Fig. A below shows the result for chloride.

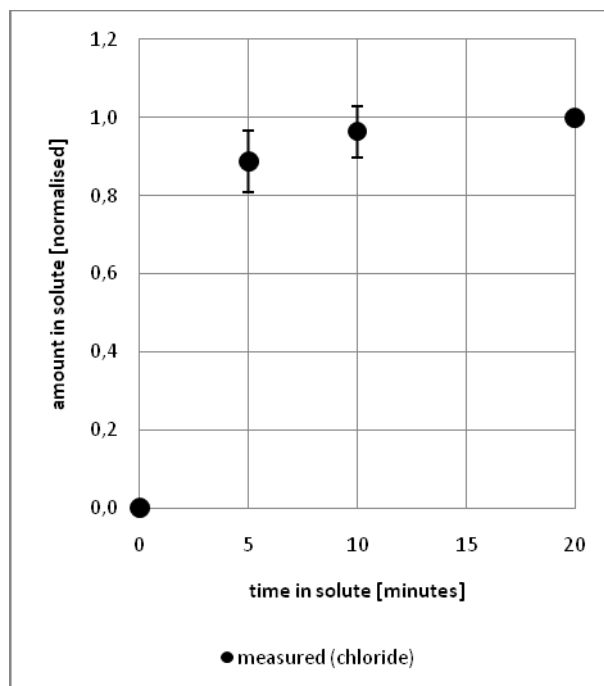


Figure A. Overview of all chloride wash-off data. For each wash-off sequence, data have been normalised to the amount in the solute measured after 20 minutes. Vertical bars denote standard deviations.

Nevertheless, we realize that our statement (“...important insights into the wash-off dynamics, for instance, in terms of reaction constants”) is not well worded and would need revision, for example into “Although the methodology was not primarily aimed at determining reaction constants, our data suggest opportunities for further developments towards that end. If so, more and smaller measurement-time intervals are needed. However, such further studies can benefit from our findings, which establish that wash-off durations below about 5 minutes should then be in focus.”

However, one needs to bear in mind that our basic quest here was to find an optimal time duration for keeping the leaves in the solute (a duration long enough to ensure that NaCl be washed off but small enough to avoid that other processes would come into play, such as leaves being softened-up in the solute and beginning to leach substances from the internal biological fabric; and also small enough to make the overall procedure labour-effective). As observed by for instance Oliva et al. (2003) [see below], any combination of leaves (or needles), substance to be washed off, and solute, needs such study to establish optimal wash-off durations particular to the combination. We definitely feel that our findings constitute a helpful contribution for the combination of *Q.r.* leaves, NaCl, and de-ionized water. [Oliva, R.S., and Raitio, H.: Review of cleaning techniques and their effects on the chemical composition of foliar samples, *Boreal Environmental Research*, 8, 263-272, 2003.]

In addition, our methodology involves steps towards “fingerprinting” the aerosol. Although a matter not raised by the Referee, we observe that, in principle, also that aspect of the methodology can be further developed (such as through using more than two suitable ions in the solution used for aerosol generation).

As the Referee states (see also below): “Clearly, for NaCl aerosol most of the deposited material is washed off within 5 - 10 min.” We observe that without our data, that statement would not have been possible.

**Referee comment: Is there a physical explanation for the assumption of first-order wash-off dynamics?**

Authors' response: First, we would like to point out that our Eqs. 3a and 3b, in the submitted version, in themselves provide a physical description of a typical washing process, as already observed above. Such processes are in some respects analogous to for instance the discharging/charging of a battery. Our perception of the process is that as the leaves are submerged into the solute, the aerosol-borne NaCl particles (in our case most likely droplets, in view of the relative humidity conditions in the tunnel) deposited on the leaf surfaces essentially instantaneously dissolve within a diffuse double-layer enveloping the leaf, whereupon exchange commences with the surrounding media, in particular the solute. While a mathematical description of that exchange over the first few minutes (or less) may well be open to debate, the major time period thereafter should be well (albeit perhaps not perfectly) captured by our Eqs. 3a and 3b. We return to this matter in conjunction with Fig. B below.

We also observe that the behaviour of the data in Fig. 3 (high-exposure) in relation to that in Fig. 3 (low exposure) is consistent with the general kinetics in physico-chemical systems in that reactions generally proceed more rapidly as the concentrations of the reactants are increased. (After high exposure, the amount of NaCl on the leaf surface is higher, so that – as the Referee observes – the transfer from the surface into the solute is faster, with the result

that “solute concentration is more or less constant for the three different measurements [at 5, 10, and 20 minutes]”).

We also note that 1<sup>st</sup>-order reactions are the most commonly employed ones in modelling environmental chemistry processes (including transfer of substance from one compartment to another), and that this is quite logical an approach. It also results in equations that are more transparent to discussion (and criticism) and that avoid often unnecessary complications in view of the practical objectives at hand.

Although many reactions may come sufficiently close to first-order reactions, their description as being so might often be approximations (probably, the only “perfectly” first order process is radioactive decay). We therefore explored a range of other possible kinetics. These could potentially involve 2<sup>nd</sup> order reactions, fractional-order reactions, consecutive-reaction dynamics, reversible-reaction dynamics, and Michaelis-Menten (or Monod) types of kinetics. Among these, the main candidates in our case (in addition to 1<sup>st</sup> order kinetics) would be fractional-order kinetics (not uncommon in dissolution reactions) and 2<sup>nd</sup> order kinetics (often a relevant model in atmospheric gas-phase reactions).

A general expression is, with  $m(t)$  denoting the amount of the substance on the leaf surfaces, and  $M(t)$  the amount of the substance in the solute:

$$dm(t)/dt = -k [m(t)]^p \quad (3a')$$

$$dM(t)/dt = k [m(t)]^p \quad (3b')$$

where  $p$  is the order of the reaction (fractional if  $p$  has a non-integer value) and  $k$  is a reaction constant (the dimension of which is defined by  $p$ ). This system of differential equations is analytically tractable, and  $k$  and  $p$  can be varied to explore the behaviour of  $M(t)$  in relation to our data.

For instance, it might be hypothesised that the surface of the deposited particles (rather than their mass) controls the exchange of mass ( $m$ ) with the solute as a function of time  $t$ , at least during the initial stage. If so (and if the density of the particle is  $1 \text{ g cm}^{-3}$ ),  $p$  would take the value  $2/3$ , and the value of  $k$  can be calculated to meet the condition that  $M(t)$  reaches a certain value at  $t = 20$  minutes (which in Fig. A is  $I$ ). Another possibility would be 2<sup>nd</sup>-order dynamics (i.e.,  $p = 2$ ), with the value of  $k$  calculated according to conditions set by for instance  $M(5)$  or  $M(10)$ (cf. Fig. A).

Also, for 2<sup>nd</sup>-order kinetics Eqs. 3a' and 3b' can be extended to include a 1<sup>st</sup>-order term:

$$dm(t)/dt = k_1 [m(t)]^2 - k_2 m(t) \quad (3a'')$$

$$dM(t)/dt = -k_1 [m(t)]^2 + k_2 m(t) \quad (3b'')$$

For certain value-ranges of the reaction constants  $k_1$  and  $k_2$ , this system of differential equations will yield a sigmoid-type  $M(t)$  function (not uncommon in modelling for instance sorption reactions)

Solutions to  $M(t)$  that result from the above considerations are shown in Fig. B. Fig. B clearly suggests that  $2/3$ -order dynamics (and, implicitly, also dynamics of order  $0 \leq p < 2/3$ ) cannot

capture the behaviour of the wash-off process in our case. 2<sup>nd</sup>-order dynamics cannot be excluded, although time durations much larger than 20 minutes are needed for  $M(t)$  to approach the required value at  $t = 20$  as close as does the 1<sup>st</sup>-order dynamics curve. The extended 2<sup>nd</sup>-order formulations can also not be excluded. Whether or not 2<sup>nd</sup>-order approaches are better than a 1<sup>st</sup>-order approach may be open to debate until additional data pertaining to time durations smaller than 5 minutes become available. A salient point remains, however, with respect to the fact that our approach shows that the washing time needed to determine the amount deposited should be at least 10 minutes in our case if desired uncertainties are to be less than about 5 to 10%, and that a measuring step also after 20 minutes is necessary to check whether additional washing time would be appropriate. In addition, Fig. B shows that a 1<sup>st</sup>-order model works as well for the interval  $5 < t < 20$  minutes as do 2<sup>nd</sup>-order approaches, and better describes the asymptotic behaviour.

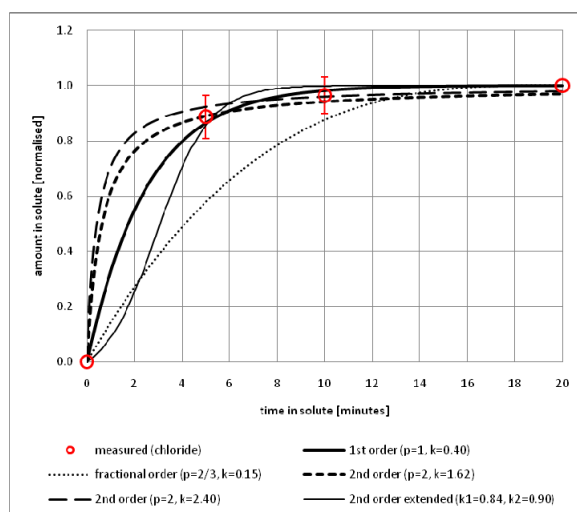


Figure B. Comparison between 1<sup>st</sup>-order ( $p = 1$ ), fractional order ( $p = 2/3$ ), basic 2<sup>nd</sup>-order ( $p = 2$ ), and extended 2<sup>nd</sup>-order (see main text) kinetics in relation to our experimental data. The dimension of  $k$  is  $[\text{mass}^{(1-p)} \text{ per s}]$ . Initial conditions for solving Eqs. 3a' and 3b' are  $m(0) = 1$ ,  $M(0) = 0$ . Note that for  $0 < p < 1$ ,  $m(t)$  and  $M(t)$  are only mathematically defined up a critical time  $t_{crit} = m_0 (1-p)/[(1-p) k]$ , so that for  $p = 2/3$  the curve shown is the only one that meets the requirement  $M(t) \rightarrow 1$  as  $t \rightarrow 20$ . For the basic 2<sup>nd</sup>-order curves to come as close to the value 1 as does the 1<sup>st</sup>-order function for  $t = 20$ ,  $t$  needs to be larger than 1000 minutes.

**Referee comment: [W]hat is the advantage of the model fit over the ion concentration measurement after 20 min? In order to obtain an estimate of the washed-off ion concentration, is there a significant difference if the ion concentrations measured directly after 20 min (as presented in Figs. 2 and 3) are compared with the corresponding  $m(0)$  values in Tab. 1 and 2?**

Authors' response: First, as mentioned above, the measurement after 20 minutes was necessary to establish a safe upper time limit for the washing. That measurement also helps constrain the fitting procedure (although, as already noted above, measurements also after time durations smaller than 5 minutes would have been desirable).

There is no statistically significant difference between  $M(20)$ -values and  $m(0)$  values. However, it merits mention that the curve-fit can be seen initially as a purely mathematical procedure wherein a mathematical function is adapted in an optimised manner to the data points, and the goodness of the fit (the standard deviations of the predicted  $m(0)$ -values) then offers a means for estimating uncertainty. The mathematical function used is quite a

reasonable one to choose for that purpose, irrespective of whether or not the function can be given a physical underpinning. Again, it should be observed that the data points at  $t = 0$  minutes are well defined by the methodology's pre-exposure measurement. As it happens, the function also represents 1<sup>st</sup>-order kinetics. As shown by Fig. B, 2<sup>nd</sup>-order kinetics might instead be at hand, but the general tendency that  $M(t)$  stabilizes as  $t \rightarrow \infty$  would still remain. However, in view of our quest for suitable washing-time durations, the essential point is not the time interval below 5 min (except the representative of a  $t = 0$  measurement, i.e. the pre-exposure wash-off step) but the steps  $> 5$  minutes. Without these steps, there would be no guarantee that wash-off was completed.

However, since the  $M(t = 20)$  measurements ensure that the wash-off process is complete, and since the analytical uncertainty in the  $M(20)$  values is of the same magnitude as the uncertainty which is given for  $m(0)$  from the curve fits, we agree that – from that particular perspective – our contribution could be simplified. A major result of the study – as the Referee formulates it: “Clearly, for NaCl aerosol most of the deposited material is washed off within 5 - 10 min.” – would not change. An option could therefore be to re-shape our paper into a fairly brief technical note. On the other hand, such a note would quite likely receive criticism for not framing the experimental data in a discussion of what dynamics that could be involved.

**Referee comment: Overall, the presented approach should be tested with sampling times more adequate for characterizing the wash-off dynamics. Clearly, for NaCl aerosol most of the deposited material is washed off within 5 - 10 min.**

Authors' response: As is obvious from our responses above, we agree that further studies would be needed for exploring the detailed dynamics in the time interval  $0 < t < 5$  minutes. We also appreciate the Referee's basic view that the wash-off is essentially completed after some 10 minutes. Clearly, our  $M(20)$  measurements were necessary to enable that conclusion.

**Referee comment: The observed retention of sodium is well-known but additional insight could be gained, e.g. if the authors followed up on the studies of Neinhuis and Barthlott (1998) discussed on p. 3863.**

Authors' response: We certainly appreciate the Referee's suggestion. As is obvious in our manuscript (see for instance our discussion and several references on p. 3855, line 27 and p. 3856, lines 6-7), we agree with the Referee that sodium retention as such is well-known. Additional studies on that subject could of course be referred to in our manuscript. However, to our knowledge, the number of studies regarding foliar retention of aerosol-borne sodium in experimental set-ups of the kind we use is limited (i.e., with respect to oak leaves exposed to aerosol-borne NaCl with a defined particle-size distribution). Sodium is a metal and should therefore be expected to show a special affinity for organic material such as epicuticular waxes that are present at the surface of oak leaves. As we observe in our manuscript, Neinhuis & Barthlott (1998) note the importance of leaf micro-morphology and wettability for the collection of contaminating particles by oak leaves. Oak wax platelets could be more susceptible to alterations due to their shape and chemical composition (formed by primary alcohols). Because oak leaves do not maintain water-repellency over a growth season, waxes tend to transform to amorphous wax layers that provide a more retentive surface for particles.

Unfortunately, the reference to Neinhuis & Barthlott (1997) on page 3863, line 27 is missing in our list of References, and is: Neinhuis, C. and Barthlott, W.: Characterization and

distribution of water-repellent, self-cleaning plant surfaces, *Annals of Botany*, 79, 667-677, 1997. We also note that Neinhuis et al. (2001) [see below] provide methodologies and solutes suitable for the extraction of waxes on leaves (including from *Q.r.*) and also show, with the use of among others Scanning Electron Microscopy, how wax platelets are geometrically organised and that their dimensions are in the  $\mu\text{m}$  range. Such information, in addition to that given by Neinhuis & Barthlott (1998) and by the highly interesting (and somewhat contrasting) studies by Burkhardt (2010) [see below] and Bargel et al. (2006) [see below], is undoubtedly of substantial interest to the further understanding of aerosol-deposition processes. [Neinhuis, C., Koch K., and Barthlott, W.: Movement and regeneration of epicuticular waxes through plant cuticles, *Planta*, 213, 427-434, 2001; Bargel, H., Koch, K., Cerman, Z., and Neinhuis, C.: Structure–function relationships of the plant cuticle and cuticular waxes — a smart material? *Functional Plant Biology*, 33, 893–910, 2006; Burkhardt, J.: Hygroscopic particles on leaves: nutrients or desiccants? *Ecological Monographs*, 80 (3), 369–399, 2010.]

**Referee comment: [Finally,] it is absolutely essential to clarify the added benefit of the presented modified leaf-washing technique with regard to aerosol/forest interactions (p. 3852), aerosol deposition to plant material (p. 3864), and aerosol deposition modeling (p. 3865).**

Authors' response: In principle, and as discussed in the introductory part of this Authors' response, we agree that the framing and title of our methodology contribution would need re-thinking. However, attending to the particular aspects raised in this final comment by the Referee would necessitate a much longer manuscript. On the other hand, some other recommendations (with respect to details of the kinetics and leaf surface properties) also provided by the Referee would rather lead to the conclusion that a brief technical note would better pin-point the essence of our findings. These findings include the usefulness of an inexpensive, simple-to-handle, and harmless tracer for laboratory-based studies of leaves exposed to an aerosol.

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