Abstract: A model is presented for the Na+ and K+ levels in the irrigation water of greenhouses, specifically those for the cultivation of tomato. The model, essentially based on mass balances, not only describes the accumulation of Na+ but includes a membrane unit for the selective removal of Na+ as well. As determined by the membrane properties, some of the K+ is removed as well. Based on real-life process parameters, the model calculates the Na+ and K+ concentration at three reference points. These process parameters include the evapotranspiration rate, the K+ uptake by the plants, the Na+ and K+ content of the fertilizer, the Na+ leaching out from the hydroponic substrate material, and the Na+ and K+ removal efficiency of the membrane unit. Using these parameters and given a constant K+ concentration of the irrigation water entering the greenhouse of 6.6 mM (resulting in the optimal K+ concentration for tomato cultivation), the composition of the solution is completely defined at all three reference points per irrigation cycle. Prime aim of this investigation is to explore the requirements for the selective membrane that currently is developed in our lab. It is found that even for a limited Na+ over K+ selectivity of 6, after a number of cycles the Na+ level reaches steady state at a level below the upper (toxic) threshold for tomato cultivation (20 mM). Economic aspects and ways of implementation of such a system are briefly discussed.
Leeuwarden, March 2nd, 2018

Dear Editor,

Thank you so much for giving us the opportunity to submit a revised version of our manuscript titled “Modelling the Selective Removal of Sodium Ions from Greenhouse Irrigation Water Using Membrane Technology”, authored by Zexin Qian et al. We feel grateful to the Reviewers as well and think that their valuable comments really improved the paper.

Please find attached the revised manuscript as well as a point-to-point reply to the specific comments of each Reviewer. Most notable changes accordingly the suggestions of the Reviewers are 1) Reduction of number of figures, from 6 to 4, 2) an outline of currently existing Na+ selective membranes and their limitations, 3) a Supplement containing most of the model equations, as well as their derivation and 4) a more detailed economic evaluation, including both capital costs as power consumption.

Thanks again for re-considering our revised manuscript for publication in Chemical Engineering Research and Design.

Sincerely,

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Point-by-point reply to the reviewers’ reports

>>We thank the reviewers for their time and constructive comments. Please note: the regular text (in black) is taken from the reviewers reports whereas our reply is printed in red, starting with >>. The line numbers we refer to are highlighted in the manuscript.

Reviewer: 1

The manuscript submitted investigates modeling selective removal of sodium ion from greenhouse irrigation water using membrane separation. Generally, the manuscript is rich, comprehensive and well written. The results are useful for membrane selection for industrial application. The manuscript in its current form is acceptable and well structured, yet, needs minor improvements. Here are some recommendations to further improve the manuscript:

>>We appreciate the reviewer’s positive recommendation, his/her acknowledgment on the comprehensiveness of our work and valuable suggestions for further improvement. Based on the feedback we have made several substantial changes to the manuscript as indicated below.

1. It has been noticed the use of words like "we" and "our" repeatedly in the manuscript. I suggest using passive tense to avoid use of such terms in high-quality scientific work like this one.

   >>We followed the suggestion of the Reviewer and used the passive tense instead.

2. Regarding Figure 5, page 19, I think it would be better to present the y-axis in log numbers. Doing this, authors will not need to show a zoomed part of the lower left corner of the figure as currently indicated.

   >>Also in response to the second Reviewer, the Results section has now be totally revised by showing all the data in just two figures. By reducing the range of considered membrane selectivity the need to plot the data in log numbers disappeared.

3. In the recommendation, it would be an added value if the authors would survey the membrane market and recommend one or two membrane types that are currently available that meet the Na+ and K+ selectivity requirements indicated in this work.

   >>We fully agree and address this issue in lines 61-78. Additional remarks but in a slightly different context can be found in lines 173 - 178 and 393-402. We also added references 13-21 regarding membrane technology, with 5 out of 9 published in 2016 or later (see also point #1 of Reviewer 2).

Reviewer: 2
Nice paper, presumably a summary of an MSc thesis. English OK, sometimes greenhouse instead of greenhouse. But some issues need to be addressed and some reorganisation is recommended, as some things that are presented seem irrelevant and unmotivated.

>>We appreciate the reviewer’s positive evaluation of the manuscript and for the most useful comments. We followed by far the most of the valuable suggestions. Please find below our point-by-point response.

1. Not much recent literature is referred to; only 2 references more recent than 2010. Membrane separations is an active field, developments are fast!
   >>We fully agree and address this issue in lines 61-78. Additional remarks but in a slightly different context can be found in lines 173 - 178 and 393 - 402. We also added references 13-21 regarding membrane technology, with 5 out of 9 published in 2016 or later (see also point #3 of Reviewer 1).

2. It seems that the actual problem is the high Na content in the fertilizer (line 104) - can’t that be improved?
   >>This remark made us reconsider the sources of Na+ entry. We added a calculation of the amount of Na+ entering the system, see lines 330 - 337. As can be concluded from this calculation, the leaching from the substrate contributes most to the amount of Na+ entering the IW system. So even if the Na+ content of the fertilizer could be drastically reduced, Na+ still accumulates in the (recycled) IW but at a lower rate. See also lines 351 – 354.

3. Also, it may be a good / better idea to lower the Na+ content of the rainwater used, using a reverse osmosis membrane process.
   >>Please see the comment on the previous question.

4. line 51: similar size.... well I would say that the larger size of K+ is a key to separate it from smaller Na+. For example using a zeolite...
   >>The Reviewer is absolutely correct that certain zeolites do indeed show sieve properties and do distinguish between cations of different size. However, those applications refer to absorbance- rather than membrane-based technology. Our aim is to go for the latter because in this way the inevitable regeneration step of the resin after it has been saturated with Na+ is avoided, see lines 57 – 60.

5. Figure 1: give some values for the input and output streams, what are we talking about?
   >>We followed this good suggestion and added the volumetric flows to Figure 1.

6. line 117: zero water transportation through the membrane ?? I mistake I guess; water will go through the membrane carrying the Na+, K+ ions....
   >>The very hydrophobic nature of the Liquid Supported Membrane (LSM) we currently develop implies an essentially zero water permeation. This issued is addressed in lines 173 – 178.

7. line 126-131: so the concentration K+ increases from 6.6 to 11.4 mM in the greenhouse "process" - but that is more than the 6.6 mM that the plants want?
The Reviewer is absolutely right, as formulated this statement was prone to misunderstanding and confusion. The optimal K+ concentration of 6.6 mM (advised by our ‘greenhouse and fertilizer’ partners van der Knaap and Yara) refers to the K+ content of the incoming water (i.e., at point #0 in Figs. 1 and 2). This is now clearly explained in lines 126 – 129 (and again mentioned in lines 150 – 152).

8. line 142: so 13.5 mM Na+ leaves the greenhouse, but that means that in the greenhouse (where this comes from) the concentration is much higher than the threshold? It seems that the black box Greenhouse (Green House) is not well described? What do the plants (tomatoes) get, compared to what is leaving the greenhouse?

>>Again, we fully agree with the Reviewer on this crucial point. As is true for the optimal K+ concentration in the previous question, a more detailed explanation is even more important for the threshold Na+ concentration. The level at which Na+ becomes detrimental for tomato cultivation is set at 20 mM (again, as advised by van der Knaap and Yara). Given the evapotranspiration and the Na+ leaching out the substrate, this 20 mM threshold in the greenhouse translates into a Na+ level of the incoming water at point #0 of (rounded-off) 4 mM. See lines 129 and 217 – 222. In addition, Fig. 4 now shows the Na+ level of both the incoming water (A) and the water leaving the greenhouse (B).

9. detail in Figure 2 greek symbol zeta is used in stream 2, in the text symbol xi is used (and xi + epsilon = 1)

>>This has been corrected in the present revised version.

10. section 2 An enormous amount of straightforward mass balance equations are given. Please move more of these to Supplementary Information, or produce a Table (which could take half a page) where the equations are collected. It looks impressive but most is trivial; it takes too much space.

>>The Reviewer argues that the manuscript occupies too much space. Therefore, we followed the advice of the Reviewer in putting a substantial amount of model explanation (in particular regarding the second cycle) in a Supplement (see line 293). In addition, we reduced the number of figures from 6 to 4 (see also points 13 & 14).

We disagree however on one point with the Reviewer in that all mass balance equations are too trivial to show in the main text. We really think that taken them out seriously impairs the paper and that the reader deserves a clear explanation where the numbers come from. We do show the generalized expressions 17 and 18 because Figs. 3 and 4 were constructed with the help of these expressions (see line 291 – 293).

11. line 195 typo uses -- used.

>>Thanks to the reviewer, it has been corrected in the present revised version.

12. page 10-13: see comment 10: I also assume that the authors carefully checked these equations...

>>We double checked all equations and actually did find a small mistake in the expression for the Na+ content of the water leaving the greenhouse. Even though the story remains essentially the same, the data shown in Figs. 3 and 4 slightly changed, as well as the
conclusion that given a 10% loss of K+, a Na+ over K+ permeation selectivity of 6 suffices
(instead of 7 previously).
In addition, we explicitly state that the generalized expressions 17 and 18 can be reduced to
Eqs. 13 and 14 (lines 298 – 299). The calculations for Figs. 3 and 4 were performed both
ways, first, from cycle to cycle and, secondly, using the generalized Eqs. 17 and 18. Either
way, the results were the same.

13. page 15-17, and Figure 3: what is the point in addressing values gamma < 1? That
means accumulating Na+ rather than K+ while Na+ is enriched already in the greenhouse
process. Makes no sense: remove this from the paper, and focus on high values for alpha
(for Na+) and small values for beta (for K+). Already beta = 0.9 seems to be an unfeasible
high number to start with.
>>Point taken from the Reviewer, this part has been taken out completely.

14. line 340: not discriminating... which means gamma = 1: makes no sense, useless. See
above. Gamma should be >> 1, as the authors show later. Start section 3 with a discussion
on what minimum value for gamma is needed. Also skip sentences like line 345 Increasing
... accumulation: of course, it is all very obvious. Don’t waste the readers time (and the
paper this article is maybe eventually printed on). The reader probably has a degree in
chemical engineering!
>>Point taken from the Reviewer, this part has been taken out completely.

15. line 366: and what is the value for Na+ added?
>>The Na+ entering the system from different sources is now explained in lines 330 – 337.
See also question #2 of this Reviewer.

16. figure 5: add lines for gamma values 7,8,9. There it becomes interesting / useful for
the reader, for an acceptable ChERD paper.
>>We fully agree, this substantially clarifies the figure.

17. page 19-20: do membranes exist that can give the properties needed?
>>There are no currently existing separation (i.e., for high fluxes) membranes that can
discriminate between two ion species of equal valance. This information has been added to
the text (lines 61 – 71), as well as the type of membrane we aim for (lines 72 – 78 and lines

18. line 397: what would be capital costs for this 10 cells stack, roughly, and what would
be electricity consumption for processing, say as kWh per m3 processed (fed to the
membrane)
>>Even though it remains an intelligent guess rather than an accurate prediction, we thank
the Reviewer for this valuable suggestion and agree to pay more attention to this issue.
Capital costs are discussed in lines 393 – 402 and 417 – 421 and power consumption in lines

19. line 432: note that the final decision for use or not is dictated by profit margins.
Minimising costs is not enough; profit is needed. Or do you mean that subsidies may be
used to turn a cost into a profit?
>>We mean that the future cost for discharge should be taken into account as well, see lines
422 – 427.
20. Conclusions: you may mention that cleaning the fertilizer, lowering the Na+ content, should be considered too.

As argued, the Na+ concentration increase due to leaching equals 285 g/hr, far more than the Na+ entering the system from the fresh water and fertilizer, 3 and 72 g/hr, respectively. See lines 351 – 354 and question #2 of this Reviewer.
• Simulation of Na⁺ and K⁺ concentration in recycled closed-loop irrigation water.
• Development of a membrane-based system for the removal of excess Na⁺.
• Permeation selectivity of 6 suffices to maintain the system under Na⁺ threshold.
• Implementation of an electro-dialysis like set-up.
• Required membrane surface area around 70 m².
Modelling the Selective Removal of Sodium Ions from Greenhouse Irrigation Water Using Membrane Technology

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Abstract

A model is presented for the Na⁺ and K⁺ levels in the irrigation water of greenhouses, specifically those for the cultivation of tomato. The model, essentially based on mass balances, not only describes the accumulation of Na⁺ but includes a membrane unit for the selective removal of Na⁺ as well. As determined by the membrane properties, some of the K⁺ is removed as well. Based on real-life process parameters, the model calculates the Na⁺ and K⁺ concentration at three reference points. These process parameters include the evapotranspiration rate, the K⁺ uptake by the plants, the Na⁺ and K⁺ content of the fertilizer, the Na⁺ leaching out from the hydroponic substrate material, and the Na⁺ and K⁺ removal efficiency of the membrane unit. Using these parameters and given a constant K⁺ concentration of the irrigation water entering the greenhouse of 6.6 mM (resulting in the optimal K⁺ concentration for tomato cultivation), the composition of the solution is completely defined at all three reference points per irrigation cycle. Prime aim of this investigation is to explore the requirements for the selective membrane that
currently is developed in our lab. It is found that even for a limited Na\(^+\) over K\(^+\) selectivity of 6, after a number of cycles the Na\(^+\) level reaches steady state at a level below the upper (toxic) threshold for tomato cultivation (20 mM). Economic aspects and ways of implementation of such a system are briefly discussed.

**Keywords**
Greenhouse; Irrigation water; Sodium removal; Mass balance; Modelling; Na\(^+\) over K\(^+\) membrane selectivity

**1. Introduction**
Closed-loop soilless or hydroponic systems are already widely used if not, at least in certain countries e.g. The Netherlands, common practice in horticulture[1]. Nutrients and water are supplied continuously to the irrigation water (IW) to compensate for nutrient uptake by the plants and water loss due to evapotranspiration. Ideally, the nutrient and water supply are fine-tuned such that the nutrient concentration and the osmotic pressure of the drainage solution remain (fairly) constant. Consequently, nutrients, which are present but are not taken up by the plant, accumulate in the IW. Na\(^+\) is a typical example of an ion that over time builds up in the IW [2]. High Na\(^+\) levels inhibit plant growth directly or indirectly by hampering the uptake of other nutrients [3-6]. Because of the detrimental effects of high Na\(^+\), the IW Na\(^+\) level has been subject of numerous studies already [7-9]. These studies are restricted however to simulation studies, validated or not by monitoring the actual Na\(^+\) level in the IW during crop growth. Despite the detrimental effects at higher levels, plants do show a certain tolerance for Na\(^+\). Reported Na\(^+\) threshold values for tomato vary somewhat but levels above 5 dS/m, equivalent to 50 mM, prove to inhibit growth and yield [10]. The threshold value might
depend on the tomato species; the value used in the present study is 20 mM. As soon as 
Na$^+$ exceeds the threshold level, the IW is discharged and needs to be renewed. After 
replenishing the system with freshly prepared IW the entire process of Na$^+$ building up 
starts all over again. Our goal is, apart from monitoring, to develop a (membrane-based) 
system that selectively removes accumulated Na$^+$ from the IW. A complication arises 
from the fact that K$^+$, an essential plant nutrient, has very similar physicochemical 
properties as Na$^+$. Both (alkali metal) ion species have the same valence (+1) and are 
similar in size with ionic radii of 1.90 and 2.43 Ångstrom for Na$^+$ and K$^+$, respectively. 
However, a key (physiological) difference between the two ion species is that Na$^+$ is 
hardly taken up by the plant and is the major cause of salinity toxicity [11, 12]. Excess 
Na$^+$ thus needs to be removed, either by resin-based absorbance technology or 
membrane technology. The latter is preferred because it circumvents the necessity of 
resin regeneration once it has become saturated with Na$^+$.

The fact that Na$^+$ and K$^+$ behave very much the same because they share similar 
physicochemical properties is exactly the reason that there are no commercial 
separation membranes available yet that discriminate between the two ion species. Here 
separation refers to a membrane that allows high fluxes. Selective membranes for ion 
selective electrodes (ISE) do exist already. However, ion fluxes over such potentiometric 
membranes are by definition essentially zero [13, 14]. Ceramic NASICON-based 
membranes do selectively transport Na$^+$ [15]. However, only harsh operational 
conditions like high temperature or high acidity or alkalinity justify their use because of 
the high price. In addition, the high conductivity demonstrated in battery applications 
remains relatively low compared to the conductivity of typical polymeric ion exchange 
membranes [16].
To impose selectivity on a polymeric or Liquid Supported Membrane (LSM), a compound is blended in with the membrane polymer or a mobile carrier is added to the organic phase of the LSM [17, 18, 19]. Na\(^+\) selective carriers include natural monensin and the synthetic crown ether 15-crown-5. Monensin has been used for ISE applications as well as for Na\(^+\) extraction by ionic liquids enriched with monensin [20, 21]. Current focus of our lab is on developing a LSM-based system with the organic phase supplemented with 15-crown-5.

The technological challenge thus is to develop a separation membrane that permeates Na\(^+\) but not, or at least to a much lower extent, K\(^+\). Obviously, the less permeable for K\(^+\), the less K\(^+\) needs to be re-supplied to compensate for this loss. Therefore, a key question for the membrane-to-be-developed concerns its required Na\(^+\) over K\(^+\) permeation selectivity. Crucial here to realize is that there is no need to remove all Na\(^+\). Instead, all that needs to be achieved is a (steady-state) concentration of Na\(^+\) below the threshold for, in this case, tomato cultivation. Apart from the fact that total Na\(^+\) removal is technologically hardly feasible, it can be expected as a rule of thumb that the higher the membrane selectivity, the higher the investment costs will be. On the other hand, the higher the selectivity the lower the costs for K\(^+\) re-supply and, evenly important, the more sustainable the overall technology. Prime aim of the present study is to explore the required membrane specifications in terms of Na\(^+\) over K\(^+\) permeation selectivity and K\(^+\) and Na\(^+\) permeability and flux, given real-life operational process parameters (e.g., K\(^+\) uptake by tomato, optimal K\(^+\) level in the IW, evapotranspiration). The simulation study presented here is based on the calculation of the K\(^+\) and Na\(^+\) levels at three different reference locations in the IW system and during subsequent cycles of operation. The prime criteria for the optimal membrane characteristics will essentially be based on the largest number of cycles the system can operate continuously at the lowest possible
The membrane specifications resulting from the present analysis will guide us in the currently performed investigation to actually fabricate such a membrane system.

2. Material & Methods

2.1 System & Model Design

The greenhouse recycling system considered in the present study is schematically shown in Fig. 1. The fresh water source is accumulated rainwater whereas dissolved fertilizer is added as stock solution with a composition adjusted to the requirement of the particular greenhouse crop. Also indicated in Fig. 1 is the membrane unit responsible for Na⁺ removal and producing a waste stream of Na⁺. Depending on the membrane selectivity, this waste stream is to a more or lesser extent contaminated with K⁺. Along the process line, three reference points are distinguished: point #0 where fresh water, stock solution and recycled drain water are mixed forming fresh (i.e., next cycle) irrigation water entering the greenhouse; #1 the drain water leaving the greenhouse before it enters the membrane module and #2 the drain water after filtration by the membrane unit. The model aims to calculate the Na⁺ and K⁺ concentrations during each cycle \( n \) at the three reference points indicated. The nomenclature practiced throughout this study is based on the use of two indices, the first representing the reference point, the second the cycle number. For instance, \([K^+]_{2,3}\) refers to the K⁺ concentration at reference point #2 during the third cycle.
Figure 1. Outline of a substrate-based greenhouse irrigation water system with the drain water recycled and including a membrane unit for the selective removal of Na+. Reference points #0-2 are indicated as well as the relevant (steady-state) volumetric flows while assuming a K+ loss of 10% (i.e., β=0.1).

2.2 Process parameters

The greenhouse crop data used in the simulations were provided by Van der Knaap (The Netherlands) and (the Dutch branch of) Yara International. Van der Knaap exploits greenhouses, cultivating tomatoes; Yara is manufacturer of fertilizer. Taking into account K+ uptake by the tomato plants and evapotranspiration, the optimal K+ concentration of the IW entering the greenhouse is 6.6 mM whereas the (detrimental) threshold Na+ level of the IW in the greenhouse is set at 20 mM.

Fertilizer stock solution. Nutrients are added as dissolved salts. The fertilizer stock solution contains 9.5 mM K+ and 2.7 mM Na+ (Van der Knaap, personal communication).

Fresh water. Since rainwater is used as fresh water source at reference point #0, three sets of samples were collected during September-October-2017 at Wetsus in Leeuwarden, the Netherlands. The K+ and Na+ levels were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 5000 Series). All required dilutions were carried out with ultrapure water (Millipore...
purification unit). The average $K^+$ and $Na^+$ concentration in rain water was 158 $\mu$g/l and 2587 $\mu$g/l, resulting in background concentrations of 4 $\mu$M and 112.5 $\mu$M for $K^+$ and $Na^+$, respectively.

*Water loss (evapotranspiration).* Based on a weekly analysis of their irrigation data, over the year 2016 the average evapotranspiration in the tomato greenhouse of Van der Knaap was 63%, implying the volumetric flow at point #1 (and #2 as well with the assumption of zero water transportation through the membrane during treatment) equals 0.37 times the volumetric flow leaving point #0 and entering the greenhouse.

*K$ concentration.* $K^+$ enters the system from two potential sources:

1) The background $K^+$ concentration in fresh water (4 $\mu$M), and

2) The $K^+$ content of the fertilizer stream (9.5 mM).

Furthermore, $K^+$ leaves the system at two locations. Firstly, the nutritional $K^+$ uptake by the crops and, secondly, the loss through the membrane unit due to the given $Na^+$ over $K^+$ permeation selectivity of the membrane. Given the optimal $K^+$ concentration in the IW entering the greenhouse (6.6 mM) and the (fixed) total water loss of 63%, the fraction of added fertilizer at point #0 is adjusted to this value of 6.6 mM. The fraction of $K^+$ uptake by the plants ($\mu$) has been determined experimentally by measuring the $K^+$ concentrations of the drain water leaving the greenhouse, i.e., at reference point #1. From the measured value of 11.4 mM and the average concentration of $K^+$ entering the greenhouse (6.6 mM):

$$\mu = 1 - \frac{11.4 \times (1 - 0.63)}{6.6} = 0.36$$

*Na$ concentration.* $Na^+$ enters the system from three potential sources:

1) The background $Na^+$ concentration in fresh water (112.5 $\mu$M),
2) The Na\(^+\) content of the fertilizer (2.7 mM), and

3) The Na\(^+\) leaching from the (coconut-based) substrate material used in the greenhouse, leads to a Na\(^+\) enrichment of the irrigation water (vide infra).

Because Na\(^+\) is not taken up by the plants, it leaves the system only at the membrane unit. At the start of the first irrigation cycle the Na\(^+\) concentration in the irrigation water is 1.9 mM (resulting from the background Na\(^+\) concentrations in both fresh water and fertilizer and fixing the K\(^+\) concentration at point #0 at 6.6 mM). The Na\(^+\) leaching from the substrate was determined by measuring the Na\(^+\) concentration at point #1, and found to be 13.5 mM, resulting in a concentration increase (L) of: 13.5(1-0.63)-1.9=3.1 mM. Even though over time the Na\(^+\) is washed out the substrate, the present study assumes a constant degree of leaching during the consecutive cycles of operation.

The membrane unit needs to remove Na\(^+\) to meet a (steady-state) Na\(^+\) concentration level in the irrigation water <20 mM, i.e., the upper tolerance level for Na\(^+\) of tomato cultivation. Noteworthy, the model assumes that the membrane unit does not remove any water. The reason is that the LSM under development is composed of a hydrophobic support impregnated with a hydrophobic solvent containing the Na\(^+\) selective carrier 15-crown-5. Prior to entering this organic phase, ions need to be dehydrated with the free energy (\(\Delta G\)) of dehydration (>0) is compensated for by the \(\Delta G\) of ion coordination by the 15-crown-5(<0). The water permeation through such LSM systems is negligible.

2.3 Mass balances

At the start of each new cycle, the addition of fresh water and fertilizer at reference point #0 has to compensate for the total water loss due to evapotranspiration and K\(^+\) losses due to plant uptake and removal by the membrane unit. Together with the recycled fraction entering point #0, the fractions of added fresh water and stock solution
are adjusted such that the K\(^+\) concentration of the irrigation water entering the greenhouse at point #0 is 6.6 mM. Given this fixed value of 6.6 mM, adjustment is possible because the total fraction of fresh water and stock solution at point #0 is known to be 1.0 for the first cycle \((n=1)\), and 0.63 for all subsequent cycles \((n>1)\). The calculation of all parameters is thus based on the fraction of fertilizer stock solution \((\varepsilon)\) added at point #0. For that reason, we designated \(\varepsilon\) the master variable in our simulations. On the same token, K\(^+\) is the master ionic species, dictating, by means of \(\varepsilon\), the concentration of the slave ionic species Na\(^+\) at point #0 at the start of each new cycle. Once \(\varepsilon\) has been calculated from the mass (or volumetric flow) balance at point #0, the Na\(^+\) concentration can be calculated as well.

For the very first water cycle, only stock solution and fresh water will meet at point #0. From the second cycle on, however, recycled drain water will join these two water streams at point #0. For this reason, the calculation of the first and the following cycles should be considered separately.

**Figure 2.** Outline of Fig. 1 complemented with the volumetric flows \(\Phi_v(1)-\Phi_v(5)\) and the process parameters indicated.
2.3.1 Volumetric flow balance for the first two cycles

2.3.1.1 First irrigation cycle (n=1)

Figure 2 shows the basic outline of Fig. 1 but complemented with all relevant parameters referred to in this study. Table 1 lists all these parameters as well as their numerical value as used in this study.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_v(1)$ Volumetric flow entering the greenhouse</td>
<td>4 m$^3$/hr</td>
</tr>
<tr>
<td>$\Psi$ K$^+$ concentration in fresh water</td>
<td>4 μM</td>
</tr>
<tr>
<td>$X$ Na$^+$ concentration in fresh water</td>
<td>112.5 μM</td>
</tr>
<tr>
<td>$N$ K$^+$ concentration in fertilizer stock solution</td>
<td>9.5 mM</td>
</tr>
<tr>
<td>$M$ Na$^+$ concentration in fertilizer stock solution</td>
<td>2.7 mM</td>
</tr>
<tr>
<td>$\xi$ fraction of fresh water added at point #0</td>
<td></td>
</tr>
<tr>
<td>$\epsilon$ fraction of fertilizer stock solution added at point #0</td>
<td></td>
</tr>
<tr>
<td>$\mu$ fraction of K$^+$ entering the greenhouse taken up by the crop</td>
<td>0.36</td>
</tr>
<tr>
<td>$L$ Na$^+$ concentration increase due to Na$^+$ leaching out from the coconut-based substrate</td>
<td>3.1 mM</td>
</tr>
<tr>
<td>$\theta$ fraction of $\Phi_v(1)$ lost due to evapotranspiration</td>
<td>0.63</td>
</tr>
<tr>
<td>$\alpha$ fraction of Na$^+$ removed from the drain water leaving the greenhouse</td>
<td>0-1</td>
</tr>
<tr>
<td>$\beta$ fraction of K$^+$ removed from the drain water leaving the greenhouse</td>
<td>0-1</td>
</tr>
<tr>
<td>$\gamma$ Na$^+$ over K$^+$ permeation selectivity of the membrane unit</td>
<td>$\alpha/\beta$</td>
</tr>
</tbody>
</table>

**Table 1.** Description of the parameters used throughout this study, corresponding to Figs. 1 and 2.

Volumetric flows ($\Phi_v$) are presented as fraction of the flow entering the greenhouse, $\Phi_v(1)$ with $\epsilon$ the fraction of the stock solution and $\xi$ the fraction of fresh water. Flows $\Phi_v(2)$ and $\Phi_v(3)$ represent the volumetric flow of fresh water and stock solution added at point #0, respectively.
**Reference point #0**

As mentioned, given the optimal K$^+$ concentration for tomato and taken into account K$^+$ uptake and evapotranspiration, the K$^+$ concentration at point #0 is set at 6.6 mM. The Na$^+$ threshold of 20 mM is the maximum acceptable Na$^+$ level of the IW leaving the greenhouse. Given the Na$^+$ leaching out the substrate (3.1 mM) and the evapotranspiration (0.67), the 20 mM translates into a Na$^+$ of the IW entering the greenhouse of $20 \times 0.37 \times 3.1 = 4.3$ mM. Throughout this study the threshold Na$^+$ level at point #0 of the incoming IW is set at 4 mM.

The volumetric flow balance reads:

$$\Phi_v(1) = \Phi_v(2) + \Phi_v(3) = x_1 \Phi_v(1) + \varepsilon_1 \Phi_v(1)$$

(1)

Suppose $\Psi$ and $N$ are the K$^+$ concentration in the fresh water and in the fertilizer stock solution, respectively. Then, according to Eq. 1, the K$^+$ mass balance equals:

$$[K^+]_{0,1} \times \Phi_v(1) = \Psi \times x_1 \Phi_v(1) + N \times \varepsilon_1 \Phi_v(1)$$

(2)

Because $x_1 = 1$ and dividing by $\Phi_v(1)$ renders for the K$^+$ concentration:

$$[K^+]_{0,1} = (1 - \varepsilon_1)\Psi + \varepsilon_1 N = \varepsilon_1(N - \Psi) + \Psi$$

(3)

The fraction of stock solution thus is:

$$\varepsilon_1 = ([K^+]_{0,1} - \Psi)/(N - \Psi)$$

(4)

With $[K^+]_{0,1} = 6.6 \text{ mM}$ and $\Psi$ and $N$ being known, the value of $\varepsilon_1$ is defined.

Once $\varepsilon_1$ is known, the Na$^+$ concentration for the first cycle can be calculated by:

$$[Na^+]_{0,1} = x_1 X + \varepsilon_1 M = \varepsilon_1(M - X) + X$$

(5)
where $M$ and $X$ are the Na$^+$ concentration of the stock solution and fresh water, respectively.

Compared to the K$^+$ concentration at point #0, the K$^+$ concentration at point #1 will be different due to K$^+$ uptake by the plants and evapotranspiration. Because $[K^+]_{0,n}$ is fixed at 6.6 mM, $[K^+]_{1,n}$ is directly proportional to $[K^+]_{0,n}$. Let $\mu$ be the fraction of K$^+$ taken up by the plants and $\theta$ the fraction of water loss due to evapotranspiration. Then, $[K^+]_{1,1}$ is given by:

$$[K^+]_{1,1} = [(1 - \mu)[K^+]_{0,1}]/(1 - \theta) \quad (6)$$

The Na$^+$ concentration will also change, firstly, because of evapotranspiration, secondly because of the Na$^+$ that leaches out of the coconut-based substrate used, causing an increase of the Na$^+$ concentration, represented by $L$. Then $[Na^+]_{1,1}$ is given by:

$$[Na^+]_{1,1} = ([Na^+]_{0,1} + L)/(1 - \theta) \quad (7)$$

---

**Reference point #2**

Reference point #2 is located downstream the membrane unit (permeate side) and calculation of the K$^+$ and Na$^+$ concentration at this point therefore requires implementation of the membrane characteristics. Let $\alpha$ be the fraction of Na$^+$ (compared to reference point #1) that permeates the membrane (and with that removed from the system) and $\beta$ the fraction of K$^+$ that permeates the membrane (also removed from the system). Then the K$^+$ and Na$^+$ concentrations are given by $[K^+]_{2,1} = (1 - \theta)[K^+]_{1,1}$ and

$$[Na^+]_{2,1} = (1 - \alpha)[Na^+]_{1,1},$$

respectively.
2.3.1.2 Second irrigation cycle (n=2)

The calculations for the second cycle are essentially the same as those for the first cycle. The main difference concerns the starting point, i.e., the volumetric flow balance at point #0, now given by:

\[ \Phi_v(1) = \Phi_v(2) + \Phi_v(3) + \Phi_v(5) \]  
(8)

Expressed in terms of \( \Phi_v(1) \), Eq. 8 equals:

\[ \Phi_v(1) = \xi_2 \Phi_v(1) + \varepsilon_2 \Phi_v(1) + (1 - \Theta) \Phi_v(1) \]  
(9)

Given \( \xi_2 \) \( + \) \( \varepsilon_2 \) \( + \) \( (1 - \Theta) \) = 1 \ and therefore \( \xi_2 = \Theta - \varepsilon_2 \), Eq. 9 reads:

\[ \Phi(v, 1) = (\Theta - \varepsilon_2) \Phi(v, 1) + \varepsilon_2 \Phi(v, 1) + (1 - \Theta)(v, 1) \]  
(10)

In analogy with Eq. 2, Eq. 10 results in a \( K^+ \) concentration and \( \varepsilon_2 \) at point #0 of:

\[ [K^+]_{0, 2} = \xi_2 \Psi + \varepsilon_2 N + (1 - \Theta) [K^+]_{2, 1} = (\Theta - \varepsilon_2) \Psi + \varepsilon_2 N + (1 - \Theta) [K^+]_{2, 1} \]  
(11)

\[ \varepsilon_2 = (\varepsilon^2 N - (1 - \Theta) [K^+]_{2, 1} - \Theta \Psi)/(N - \Psi) \]  
(12)

Once \( \varepsilon_2 \) has been determined, \([Na^+]| \) at each point can be calculated:

\[ [Na^+]_{0, 2} = \varepsilon_2 (M - X) + \Theta X + (1 - \Theta) [Na^+]_{2, 1} \]  
(13)

\[ [Na^+]_{1, 2} = \frac{\varepsilon_2 (M - X) + \Theta X}{1 - \Theta} + [Na^+]_{2, 1} \]  
(14)

\[ [Na^+]_{2, 2} = \frac{(1 - \alpha)}{(1 - \Theta)} [\varepsilon_2 (M - X) + \Theta X + \Lambda] + (1 - \alpha) [Na^+]_{2, 1} \]  
(15)

Apart from the fact that \([K^+]_{0,n} \) remains constant for \( n \geq 1 \) (6.6 mM), \([K^+]_{1,n} \) and \([K^+]_{2,n} \) are constant as well having (if assuming \( \Theta = 0.1 \)) a value of 11.4 and 10.3 mM, respectively. In addition, from the second cycle onwards \( \varepsilon_n \) remains constant as well and independent of
n. This can be seen after, first, substituting $\varepsilon_1$ into $[K^+]_{2,1}$ followed by substituting $[K^+]_{2,1}$ into $\varepsilon_2$, resulting in:

$$
\varepsilon_n = \frac{[K^+]_{0,n}(1-(1-\beta)(1-\mu)) - \theta \times \Psi}{N - \Psi}
$$

(16)

According to the parameter values in Table 1, $\varepsilon_n$ adopts a numerical value expressed in terms of $\beta$ of $0.25 + 0.44\beta$ ($=0.29$ for $\beta=0.1$).

### 2.3.3 Generalized expressions

As evident from Eqs. 3-5, for the first cycle $\varepsilon$ and by implication the $[K^+]$ and $[Na^+]$ as well can all be expressed exclusively in terms of the known process parameters $[K^+]_{0,1}$, $\alpha\beta\mu, \theta, r, N, M, X$ and $\Psi$. The same is actually true for the second cycle. This can readily be seen after substituting the expression for $[Na^+]_{2,1}$ into Eqs. 13, 14 and 15. Because of this, generalized expressions can be derived for $[Na^+]$ at each reference point as function of known process parameters and the cycle number $n$. The advantage of these generalized expressions is that they allow the direct calculation of $[Na^+]$ during the $n^{th}$ cycle at each reference point without the need to know (calculate) the concentrations during the previous cycles. As an example but also because Figs. 3 and 4 were constructed using these expressions, the generalized expression for $[Na^+]_{0,n}$ and $[Na^+]_{1,n}$ from the 2$^{nd}$ cycle on are given below (for their derivation, see Supplementary Information).

\[
[Na^+]_{0,n} = (M - X) \sum_{i=1}^{n} [\varepsilon_i \times (1 - \alpha)^{n-i}] + (X\theta + L) \sum_{i=1}^{n-2} [(1 - \alpha)^{i}] + (X + L)(1 - \alpha)^{(n-1)} + X\theta
\]

(17)

\[
[Na^+]_{1,n} = \frac{1}{(1-\theta)} \sum_{i=1}^{n} [\varepsilon_i \times (1 - \alpha)^{n-i}] + [(X\theta + L) \sum_{i=1}^{n-3} (1 - \alpha)^{(i-1)}] + (1 - \alpha)^{(n-3)} \times (X + L)
\]

(18)
Note that for \( n=2 \) and after a number of repeated substitutions, Eqs. 17 and 18 reduce to Eqs. 13 and 14, respectively.

**4. Results and discussion**

**4.1 Membrane selectivity**

The \( \text{Na}^+ \) over \( \text{K}^+ \) permeation selectivity also is an intrinsic membrane property. As stated previously, one of our prime goals is to determine the minimum membrane selectivity (\( \gamma \)) required to maintain the \( \text{Na}^+ \) concentration in the IW below the upper tolerance level of 4.5 mM. Because the membrane selectivity (\( \gamma \)) is defined as the ratio of its permeability towards \( \text{Na}^+ \) (\( \alpha \)) and its permeability towards \( \text{K}^+ \) (\( \beta \)), the permeation of both ion species is coupled. With both \( \beta \) and \( \gamma \) set at a fixed value, \( \alpha \) can be calculated and with that the \( \text{Na}^+ \) level at point #2, which, in turn, allows the calculation of the \( \text{Na}^+ \) level at point #0 at the start of a new cycle.

To compromise between minimizing \( \text{K}^+ \) loss and dealing with a finite membrane selectivity, the value of \( \beta \) is set (arbitrarily) at 0.1, implying that 10% of \( \text{K}^+ \) is removed together with \( \text{Na}^+ \). In combination with a membrane that does not discriminate between \( \text{K}^+ \) and \( \text{Na}^+ \) (\( \gamma = 1 \)) this results in a \( \text{Na}^+ \) removal of also 10%. In this case it is expected to see a dramatic \( \text{Na}^+ \) accumulation in the IW. Figure 3 confirms this expectation showing the \( \text{Na}^+ \) level in the IW after 10 cycles of operation and for a \( \text{Na}^+ \) over \( \text{K}^+ \) selectivity ranging from \( \gamma = 1 \) to 9. Note that \( \gamma = 1 \) indeed results in staggering \( \text{Na}^+ \) concentrations after 10 cycles of operation.
Figure 3. Accumulation of Na\(^+\) in the irrigation water entering the greenhouse (i.e., at point #0) after 10 cycles of operation for a membrane with a Na\(^+\)/K\(^+\) selectivity ranging from 1 to 9 and a K\(^+\) permeability \(\beta\) of 0.1, i.e., with 10\% - 90\% of the Na\(^+\) and 10\% of the K\(^+\) removed.

Figure 4 explores the relationship between membrane selectivity and the Na\(^+\) level at points #0 and #1 during 15 subsequent cycles of operation, given the 10\% removal of K\(^+\) (\(\beta = 0.1\)) and for a Na\(^+\) over K\(^+\) membrane permeability selectivity ranging from 5 to 9. A membrane selectivity of 5 does not suffice to achieve a steady-state [Na\(^+\)] below the threshold of 4 mM at point #0 (A) and of 20 mM at point #1 (B). Indeed, it requires at least a selectivity of 6 to accomplish steady-state levels remaining below these thresholds. As indicated in Fig. 2, Na\(^+\) is entering the system from three sources, the fresh water, the fertilizer content and the Na\(^+\) leaching from the coconut-based substrate used. As already remarked, from the second cycle on \(\epsilon_n\) adopts a constant numerical value of 0.25 + 0.44\(\beta\), i.e., 0.29 for \(\beta=0.1\). Given \(\Theta=0.63\), \(\xi\) equals 0.34, implying that the amount of Na\(^+\) entering the system from the fresh water and fertilizer is 3 and 72 g/hr,
respectively. The Na\(^+\) concentration increase due to leaching equals 3.1 mM, resulting in 285 g/hr. Evidently, at steady state the total amount of 360 gr/hr equals the amount of Na\(^+\) that needs to be removed by the membrane unit.
Figure 4. (A). [Na⁺] in the irrigation water entering the greenhouse at point #0; (B). [Na⁺] in the irrigation water leaving the greenhouse at point #1 during 15 cycles of operation, for a Na⁺/K⁺ membrane selectivity ranging from 5 to 9 and a K⁺ permeability β of 0.1, i.e., with 50% - 90% of the Na⁺ and 10% of the K⁺ removed. Dotted lines represent the threshold of 4 mM of the Na⁺ content of the IW entering the greenhouse (A) and the physiological tolerance threshold for tomato of 20 mM (B).
In order to maintain a steady-state K⁺ concentration in the IW of 6.6 mM, the added amount of K⁺, originating from the fertilizer, equals \( \varepsilon_n N \Phi_v(1) = 430 \text{ g/hr.} \)

### 4.3 Implementation

As argued in the previous paragraph, Na⁺ leaching from the substrate contributes most to the amount of Na⁺ entering the IW system, even if considering that over time this amount reduces. So even if the Na⁺ content of the fertilizer could be drastically reduced, Na⁺ still accumulates in the (recycled) IW but at a lower rate.

We envisage implementing the membrane-to-be-developed in an electro dialysis (ED)-like setting, operating under constant current conditions. From the viewpoint of capital costs, a key parameter is the total required membrane surface area (A), given the amount of Na⁺ that need to be removed. Eq. 19 gives the value of A as a function of volumetric flow through the membrane module \( Q \), the Faraday constant \( F \) (96485 C/mol), the Na⁺ concentration difference between the water entering and leaving the membrane module, the current density \( i \) and the current utilization factor \( f \) [22]:

\[
A = Q \times F \times (\text{[Na}^+\text{]}_{1,2} - \text{[Na}^+\text{]}_{2,2})/if
\]

The volumetric flow \( Q \) equals \( \Phi_v(4) = 0.37 \times \Phi_v(1) = 4.1 \times 10^{-4} \text{ m}^3/\text{s} \). As mentioned before, any water flow arising from either osmosis or electro osmosis is ignored, given the strong hydrophobic nature of the LSM system. According to Fig. 2 and given \( \alpha=0.6 \) and \( \beta=0.1 \) (Fig. 4A with \( \gamma=6 \)), \([\text{Na}^+\text{]}_{0,n}\) reaches a steady-state value of 3.45 mM. The difference between the Na⁺ concentration of the solution entering and leaving the membrane then is \( 0.6 \times (3.5 + 3.1)/0.37=10.7 \text{ mM} \). Note that this concentration difference results in \( 10.7 \times 10^{-3} \times 23 \times 4000 \times 0.37 = 365 \text{ gr Na}^+ / \text{hr} \) that needs to be removed, essentially the same amount as previously derived from the amount of Na⁺ entering the system. As
for the current density, we take a ‘typical’ value for ion exchange membranes given a total ionic strength of the incoming water of around 25-30 mM, i.e., 10 A/m² [23].

Further, as a rather conservative estimate the current utilization factor ($f$) is assumed to be 0.6, implying that 60% of the current is actually carried by Na⁺, the remaining 40% by K⁺ and other ion species present. Substituting these numbers in Eq. 19 renders a membrane surface area of 70 m². In practice, this could be achieved by constructing ED stacks with a number of cells in series. For instance, three ED modules, each comprising of a stack of 12 cells with a membrane surface area of 2 m² each.

So far our analysis has been based on average parameter values over one entire year, thereby ignoring seasonal variations. In any real-life application, the level of evapotranspiration and nutrient uptake will depend on time of the year and crop growth. This asks for a dynamic rather than static nutrient control. One option could be to monitor the water conductivity at point #1 and use this signal as input parameter for the electrode dialysis unit. This way, the recorded conductivity (as measure of the Na⁺ content) allows fine tuning of the constant current magnitude applied during operation, and with that the amount of Na⁺ (and K⁺) removed per unit time. Evidently, the implication of such dynamic control is that $\varepsilon_n$ requires re-adjustment as well.

### 4.3 Economics perspective

The specifications of the membrane-to-be developed, e.g. regarding membrane thickness and the required density of the crown ethers (as carrier molecules) in the membrane, remain elusive and await further study (in progress). Nevertheless, despite these uncertainties a few general remarks can be put forward.

Firstly, the capital cost of the LSM currently developed and validated is to a large extent dominated by the amount of 15-crown-5 needed. When purchased from TCI-Chemicals
and given the 15-crown-5 density (0.2 M), the membrane thickness (100 μm) and a support porosity of 50% the estimated cost price amounts to 78 euro per m². To put this number in perspective, the price of typical commercially available ion exchange membranes is around 30 euro per m². The most promising options to bring the price from the LSM down, seem a thinner membrane and upscaling 15-crown-5 (in-house) synthesis. It should be mentioned however that the (at this moment unknown and therefore not considered here) manufacturing cost contribute significantly to if not dominate the cost prize (Fuji Film, Netherlands; personal communication).

Secondly, the operational costs on the other hand will be dominated by the power needed to run the system. Based on the specifications of a typical ED system and given the salt concentration in the feed, the power consumption will be in the range 0.7 – 2.5 kWh/m³ [24]. The power consumption is linear with the applied current density [22] and as evident from Eq. 19, there are essentially three ways to reduce the required total membrane surface area: by reducing the volumetric flow through the system, by increasing the current utilization factor or by increasing the current density. Reduction of the volumetric flow could (possibly) be accomplished by a different configuration altogether. For instance, by positioning the membrane module not in the main stream (as in Figs. 1, 2) but instead in a bypass. This option will be explored in more detail once we (experimentally) obtained the actual specifications of our membrane under development. Improving the current utilization factor implies a higher Na⁺ over K⁺ membrane selectivity. Even though the cost for re-supplementing the IW with K⁺ will go down, the membrane itself will (probably) be more expensive due to the higher density of crown ethers required. Finally, a higher current density will reduce the total membrane surface area needed but increase the power needed during operation. As pointed out by Strathmann [22], the opposite effect of current density on required
membrane surface area and energy cost may translate in an optimal current density, resulting in the lowest overall costs.

Apart from the foregoing discussion and as remarked earlier on, the prime incentive for the current analysis was inspired more by environmental issues than by economics, even though at a certain point both types of arguments might become intertwined. For instance, (European) legislation becomes more stringent and might even aim for zero discharge in 2027, with discharge allowed only at high(er) cost [25, 26]. For now, it remains speculative how including such discharge cost will affect the overall balance.

5. Conclusion

Excess Na\(^+\) in irrigation water needs to be removed to a level dictated by the tolerance threshold specific for the particular crop, for tomato 20 mM. The closed-loop irrigation water system described here includes a membrane-based module to remove excess Na\(^+\) while preserving the (nutrient) K\(^+\) as much as possible. Based on real-life process parameters, the present study indicates that a Na\(^+\) over K\(^+\) membrane permeation selectivity of 6 already suffices to remain the Na\(^+\) level the plants are exposed to below 20 mM, at least if accepted that 10% of the K\(^+\) is removed as well. If implemented in an electro dialysis set-up while assuming a constant current density of 10 A/m², the estimated total membrane surface is 70 m². Considering the opposite effect of current density on required membrane surface area and energy cost, an optimum current density is hypothesized, resulting in a minimum of overall cost.

Conflict of Interest Statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.
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References


Supporting information

Supporting information for "Modelling the Selective Removal of Sodium Ions from Greenhouse Irrigation Water Using Membrane Technology"

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As in the manuscript, the nomenclature practiced is based on the use of two indices, the first representing the reference point, the second the cycle number. For instance, \([\text{Na}^+]_{2,3}\) refers to the Na\(^+\) concentration at point #2 during the third cycle.

The manuscript gives the equations for \(\varepsilon\) and the K\(^+\) and Na\(^+\) concentrations during the 1\(^{st}\) and 2\(^{nd}\) cycle of operation. Here the expressions for the Na\(^+\) concentrations at the three reference points during the 2\(^{nd}\) cycle are given again but, in contrast to the manuscript, this time exclusively in terms of known parameters, as required to derive the generalized expressions.

\[
\begin{align*}
[\text{Na}^+]_{2,2} &= (M - X)[\varepsilon_2 + \varepsilon_1(1 - \alpha)] + (X + L)(1 - \alpha) + \Theta X \\
[\text{Na}^+]_{1,2} &= [(M - X)[\varepsilon_2 + \varepsilon_1(1 - \alpha)] + (X + L)(1 - \alpha) + \Theta X + L]/(1 - \theta) \\
[\text{Na}^+]_{2,2} &= \\
&= [(M - X)[\varepsilon_2(1 - \alpha) + \varepsilon_1(1 - \alpha)^2] + (X + L)(1 - \alpha)^2 + (\Theta X + L)(1 - \alpha)]/(1 - \theta)
\end{align*}
\]

(1) (2) (3)

As shown in the manuscript (Eq. 16), from the 2\(^{nd}\) cycle on \(\varepsilon_n\) becomes constant:

\[
\varepsilon_n = \frac{[\text{K}^+]_{0,n}(1 -(1-\beta)(1-\mu)) - \theta \times \Psi}{N - \Psi}
\]

(4)

Apart from the fact that \([\text{K}^+]_{0,n}\) remains constant for \(n>1\) (6.6 mM), \([\text{K}^+]_{1,n}\) and \([\text{K}^+]_{2,n}\) are constant as well having (if assuming \(\theta=0.1\)) a value of 11.4 and 10.3 mM, respectively.

For this reason, this Supplement is restricted to the Na\(^+\) level at each reference point for \(n>2\).

Mass Balance for the third irrigation cycle (n=3)
In analogy with Eq. 13 in the manuscript, once $\varepsilon_3$ is known, $[\text{Na}^+]_{0,3}$ is given by:

$$[\text{Na}^+]_{0,3} = \varepsilon_3(M - \chi) + \varepsilon_2(M - \chi)(1 - \alpha) + \varepsilon_1(M - \chi)(1 - \alpha)^2 + (\chi + L)(1 - \alpha)^2 + (X\theta + L)(1 - \alpha) + X\theta$$

(5)

Likewise, in analogy with Eq. 14 in the manuscript, $[\text{Na}^+]_{1,3}$ reads:

$$[\text{Na}^+]_{1,3} = [(M - \chi) \times \varepsilon_3 + \varepsilon_2(1 - \alpha) + \varepsilon_1(1 - \alpha)^2] + (1 - \alpha)^2(\chi + L) + (1 - \alpha) \times (X\theta + L) + X\theta + L]/(1 - \theta)$$

(6)

In analogy with $[\text{Na}^+]_{2,1}=(1-\alpha)[\text{Na}^+]_{1,1}$, the $[\text{Na}^+]_{2,3}$ reads:

$$[\text{Na}^+]_{2,3} = [(M - \chi) \times \varepsilon_3(1 - \alpha) + \varepsilon_2(1 - \alpha)^2 + \varepsilon_1(1 - \alpha)^3] + (1 - \alpha)^3(\chi + L) + (1 - \alpha)^2(\chi X\theta + L) + (1 - \alpha)(X\theta + L)]/(1 - \theta)$$

(7)

Mass Balance for the fourth irrigation cycle ($n=4$)

In analogy with $[\text{Na}^+]_{2,1}=(1-\alpha)[\text{Na}^+]_{1,1}$, the $[\text{Na}^+]_{2,3}$ reads:

$$[\text{Na}^+]_{0,4} = (M - \chi) \times \varepsilon_4 + \varepsilon_3(1 - \alpha) + \varepsilon_2(1 - \alpha)^2 + \varepsilon_1(1 - \alpha)^3] + (1 - \alpha)^3(\chi + L) + (1 - \alpha)^2(\chi X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta$$

(8)

$$[\text{Na}^+]_{1,4} = [(M - \chi) \times \varepsilon_4 + \varepsilon_3(1 - \alpha) + \varepsilon_2(1 - \alpha)^2 + \varepsilon_1(1 - \alpha)^3] + (1 - \alpha)^3(\chi + L) + (1 - \alpha)^2(\chi X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta + L]/(1 - \theta)$$

(9)

Reference point #2
Mass Balance for the fifth irrigation cycle (n=5)

Reference point #0

\[ [\text{Na}^+]_{0,5} = (M - X) \times [\varepsilon_5 + \varepsilon_4(1 - \alpha) + \varepsilon_3(1 - \alpha)^2 + \varepsilon_2(1 - \alpha)^3 + \varepsilon_1(1 - \alpha)^4] + (1 - \alpha)^4(X + L) + (1 - \alpha)^3(X\theta + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta) + X\theta \]

(11)

Reference point #1

\[ [\text{Na}^+]_{1,5} = [(M - X) \times [\varepsilon_5 + \varepsilon_4(1 - \alpha) + \varepsilon_3(1 - \alpha)^2 + \varepsilon_2(1 - \alpha)^3 + \varepsilon_1(1 - \alpha)^4] + (1 - \alpha)^4(X + L) + (1 - \alpha)^3(X\theta + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta) + X\theta + L]/(1 - \theta) \]

(12)

Reference point #2

\[ [\text{Na}^+]_{2,5} = [(M - X) \times [\varepsilon_5 + \varepsilon_4(1 - \alpha) + \varepsilon_3(1 - \alpha)^2 + \varepsilon_2(1 - \alpha)^3 + \varepsilon_1(1 - \alpha)^4 + \varepsilon_1(1 - \alpha)^5] + (1 - \alpha)^5(X + L) + (1 - \alpha)^4(X\theta + L) + (1 - \alpha)^3(X\theta + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta) + X\theta + L]/(1 - \theta) \]

(13)

Generalized expressions for the n\textsuperscript{th} irrigation cycle (n\geq2)

When comparing Eqs. 1, 5, 8 and 11, the resemblance in the form of the expressions becomes evident. This resemblance allows the formulation of a generalized expression for [Na\textsuperscript{+}]\textsubscript{0,n} as function of n:

\[ [\text{Na}^+]_{0,n} = (M - X) \sum_{i=1}^{n} [\varepsilon_i \times (1 - \alpha)^{n-i}] + (X\theta + L) \sum_{i=1}^{n-2} [(1 - \alpha)^{i}] + (X + L) \times (1 - \alpha)^{(n-1)} + X\theta \]

(14)
Using the generalized form of Eq. 7 in the manuscript:

\[
[\text{Na}^+]_{1,n} = ([\text{Na}^+]_{0,n} + L)/(1 - \theta)
\]

the generalized expression for \([\text{Na}^+]_{1,n}\) is:

\[
[\text{Na}^+]_{1,n} = \frac{1}{(1-\theta)} \left[ (M - X) \sum_{i=1}^{n} [\epsilon_i \times (1 - \alpha)^{n-i}] + (X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^{i-1} \right] + (1 - \alpha)^{n-1} \times (X + L)
\]

(15)

Finally, using \([\text{Na}^+]_{2,n} = (1 - \alpha) [\text{Na}^+]_{1,n}\), the generalized expression for \([\text{Na}^+]_{2,n}\) becomes:

\[
[\text{Na}^+]_{1,n} = \frac{1}{(1-\theta)} \left[ (M - X) \sum_{i=1}^{n} [\epsilon_i \times (1 - \alpha)^{n-i+1}] + (X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^{i-1} \right] + (1 - \alpha)^{n} \times (X + L)
\]

(16)
Modelling the Selective Removal of Sodium Ions from Greenhouse Irrigation Water Using Membrane Technology

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Abstract

A model is presented for the Na\(^+\) and K\(^+\) levels in the irrigation water of greenhouses, specifically those for the cultivation of tomato. The model, essentially based on mass balances, not only describes the accumulation of Na\(^+\) but includes a membrane unit for the selective removal of Na\(^+\) as well. As determined by the membrane properties, some of the K\(^+\) is removed as well. Based on real-life process parameters, the model calculates the Na\(^+\) and K\(^+\) concentration at three reference points. These process parameters include the evapotranspiration rate, the K\(^+\) uptake by the plants, the Na\(^+\) and K\(^+\) content of the fertilizer, the Na\(^+\) leaching out from the hydroponic substrate material, and the Na\(^+\) and K\(^+\) removal efficiency of the membrane unit. Using these parameters and given a constant K\(^+\) concentration of the irrigation water entering the greenhouse of 6.6 mM (resulting in the optimal K\(^+\) concentration for tomato cultivation), the composition of the solution is completely defined at all three reference points per irrigation cycle. Prime aim of this investigation is to explore the requirements for the selective membrane that
currently is developed in our lab. It is found that even for a limited Na\(^+\) over K\(^+\) selectivity of 6, after a number of cycles the Na\(^+\) level reaches steady state at a level below the upper (toxic) threshold for tomato cultivation (20 mM). Economic aspects and ways of implementation of such a system are briefly discussed.

**Keywords**
Greenhouse; Irrigation water; Sodium removal; Mass balance; Modelling; Na\(^+\) over K\(^+\) membrane selectivity

**1. Introduction**
Closed-loop soilless or hydroponic systems are already widely used if not, at least in certain countries e.g. The Netherlands, common practice in horticulture[1]. Nutrients and water are supplied continuously to the irrigation water (IW) to compensate for nutrient uptake by the plants and water loss due to evapotranspiration. Ideally, the nutrient and water supply are fine-tuned such that the nutrient concentration and the osmotic pressure of the drainage solution remain (fairly) constant. Consequently, nutrients, which are present but are not taken up by the plant, accumulate in the IW. Na\(^+\) is a typical example of an ion that over time builds up in the IW [2]. High Na\(^+\) levels inhibit plant growth directly or indirectly by hampering the uptake of other nutrients [3-6]. Because of the detrimental effects of high Na\(^+\), the IW Na\(^+\) level has been subject of numerous studies already [7-9]. These studies are restricted however to simulation studies, validated or not by monitoring the actual Na\(^+\) level in the IW during crop growth. Despite the detrimental effects at higher levels, plants do show a certain tolerance for Na\(^+\). Reported Na\(^+\) threshold values for tomato vary somewhat but levels above 5 dS/m, equivalent to 50 mM, prove to inhibit growth and yield [10]. The threshold value might
depend on the tomato species; the value used in the present study is 20 mM. As soon as
Na$^+$ exceeds the threshold level, the IW is discharged and needs to be renewed. After
replenishing the system with freshly prepared IW the entire process of Na$^+$ building up
starts all over again. Our goal is, apart from monitoring, to develop a (membrane-based)
system that selectively removes accumulated Na$^+$ from the IW. A complication arises
from the fact that K$^+$, an essential plant nutrient, has very similar physicochemical
properties as Na$^+$. Both (alkali metal) ion species have the same valence (+1) and are
similar in size with ionic radii of 1.90 and 2.43 Ångstrom for Na$^+$ and K$^+$, respectively.
However, a key (physiological) difference between the two ion species is that Na$^+$ is
hardly taken up by the plant and is the major cause of salinity toxicity [11, 12]. Excess
Na$^+$ thus needs to be removed, either by resin-based absorbance technology or
membrane technology. The latter is preferred because it circumvents the necessity of
resin regeneration once it has become saturated with Na$^+$. The fact that Na$^+$ and K$^+$ behave very much the same because they share similar
physicochemical properties is exactly the reason that there are no commercial
separation membranes available yet that discriminate between the two ion species. Here
separation refers to a membrane that allows high fluxes. Selective membranes for ion
selective electrodes (ISE) do exist already. However, ion fluxes over such potentiometric
membranes are by definition essentially zero [13, 14]. Ceramic NASICON-based
membranes do selectively transport Na$^+$ [15]. However, only harsh operational
conditions like high temperature or high acidity or alkalinity justify their use because of
the high price. In addition, the high conductivity demonstrated in battery applications
remains relatively low compared to the conductivity of typical polymeric ion exchange
membranes [16].
To impose selectivity on a polymeric or Liquid Supported Membrane (LSM), a compound is blended in with the membrane polymer or a mobile carrier is added to the organic phase of the LSM [17, 18, 19]. Na⁺ selective carriers include natural monensin and the synthetic crown ether 15-crown-5. Monensin has been used for ISE applications as well as for Na⁺ extraction by ionic liquids enriched with monensin [20, 21]. Current focus of our lab is on developing a LSM-based system with the organic phase supplemented with 15-crown-5.

The technological challenge thus is to develop a separation membrane that permeates Na⁺ but not, or at least to a much lower extent, K⁺. Obviously, the less permeable for K⁺, the less K⁺ needs to be re-supplied to compensate for this loss. Therefore, a key question for the membrane-to-be-developed concerns its required Na⁺ over K⁺ permeation selectivity. Crucial here to realize is that there is no need to remove all Na⁺. Instead, all that needs to be achieved is a (steady-state) concentration of Na⁺ below the threshold for, in this case, tomato cultivation. Apart from the fact that total Na⁺ removal is technologically hardly feasible, it can be expected as a rule of thumb that the higher the membrane selectivity, the higher the investment costs will be. On the other hand, the higher the selectivity the lower the costs for K⁺ re-supply and, evenly important, the more sustainable the overall technology. Prime aim of the present study is to explore the required membrane specifications in terms of Na⁺ over K⁺ permeation selectivity and K⁺ and Na⁺ permeability and flux, given real-life operational process parameters (e.g., K⁺ uptake by tomato, optimal K⁺ level in the IW, evapotranspiration). The simulation study presented here is based on the calculation of the K⁺ and Na⁺ levels at three different reference locations in the IW system and during subsequent cycles of operation. The prime criteria for the optimal membrane characteristics will essentially be based on the largest number of cycles the system can operate continuously at the lowest possible
discharge of K\(^+\). The membrane specifications resulting from the present analysis will guide us in the currently performed investigation to actually fabricate such a membrane system.

2. Material & Methods

2.1 System & Model Design

The greenhouse recycling system considered in the present study is schematically shown in Fig. 1. The fresh water source is accumulated rainwater whereas dissolved fertilizer is added as stock solution with a composition adjusted to the requirement of the particular greenhouse crop. Also indicated in Fig. 1 is the membrane unit responsible for Na\(^+\) removal and producing a waste stream of Na\(^+\). Depending on the membrane selectivity, this waste stream is to a more or lesser extent contaminated with K\(^+\). Along the process line, three reference points are distinguished: point #0 where fresh water, stock solution and recycled drain water are mixed forming fresh (i.e., next cycle) irrigation water entering the greenhouse; #1 the drain water leaving the greenhouse before it enters the membrane module and #2 the drain water after filtration by the membrane unit. The model aims to calculate the Na\(^+\) and K\(^+\) concentrations during each cycle (\(n\)) at the three reference points indicated. The nomenclature practiced throughout this study is based on the use of two indices, the first representing the reference point, the second the cycle number. For instance, \([\text{K}^+]_{2,3}\) refers to the K\(^+\) concentration at reference point #2 during the third cycle.
Figure 1. Outline of a substrate-based greenhouse irrigation water system with the drain water recycled and including a membrane unit for the selective removal of Na+. Reference points #0-2 are indicated as well as the relevant (steady-state) volumetric flows while assuming a K+ loss of 10% (i.e., β=0.1).

2.2 Process parameters

The greenhouse crop data used in the simulations were provided by Van der Knaap (The Netherlands) and (the Dutch branch of) Yara International. Van der Knaap exploits greenhouses, cultivating tomatoes; Yara is manufacturer of fertilizer. Taking into account K+ uptake by the tomato plants and evapotranspiration, the optimal K+ concentration of the IW entering the greenhouse is 6.6 mM whereas the (detrimental) threshold Na+ level of the IW in the greenhouse is set at 20 mM.

Fertilizer stock solution. Nutrients are added as dissolved salts. The fertilizer stock solution contains 9.5 mM K+ and 2.7 mM Na+ (Van der Knaap, personal communication).

Fresh water. Since rainwater is used as fresh water source at reference point #0, three sets of samples were collected during September-October-2017 at Wetsus in Leeuwarden, the Netherlands. The K+ and Na+ levels were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 5000 Series). All required dilutions were carried out with ultrapure water (Millipore...
purification unit). The average K$^+$ and Na$^+$ concentration in rain water was 158 µg/l and 2587 µg/l, resulting in background concentrations of 4 µM and 112.5 µM for K$^+$ and Na$^+$, respectively.

Water loss (evapotranspiration). Based on a weekly analysis of their irrigation data, over the year 2016 the average evapotranspiration in the tomato greenhouse of Van der Knaap was 63%, implying the volumetric flow at point #1 (and #2 as well with the assumption of zero water transportation through the membrane during treatment) equals 0.37 times the volumetric flow leaving point #0 and entering the greenhouse.

K$^+$ concentration. K$^+$ enters the system from two potential sources:

1) The background K$^+$ concentration in fresh water (4 µM), and

2) The K$^+$ content of the fertilizer stream (9.5 mM).

Furthermore, K$^+$ leaves the system at two locations. Firstly, the nutritional K$^+$ uptake by the crops and, secondly, the loss through the membrane unit due to the given Na$^+$ over K$^+$ permeation selectivity of the membrane. Given the optimal K$^+$ concentration in the IW entering the greenhouse (6.6 mM) and the (fixed) total water loss of 63%, the fraction of added fertilizer at point #0 is adjusted to this value of 6.6 mM. The fraction of K$^+$ uptake by the plants ($\mu$) has been determined experimentally by measuring the K$^+$ concentrations of the drain water leaving the greenhouse, i.e., at reference point #1. From the measured value of 11.4 mM and the average concentration of K$^+$ entering the greenhouse (6.6 mM):

$$
\mu = 1 - \frac{11.4 \times (1 - 0.63)}{6.6} = 0.36
$$

Na$^+$ concentration. Na$^+$ enters the system from three potential sources:

1) The background Na$^+$ concentration in fresh water (112.5 µM),
2) The Na\(^+\) content of the fertilizer (2.7 mM), and

3) The Na\(^+\) leaching from the (coconut-based) substrate material used in the greenhouse, leads to a Na\(^+\) enrichment of the irrigation water *vide infra*.

Because Na\(^+\) is not taken up by the plants, it leaves the system only at the membrane unit. At the start of the first irrigation cycle the Na\(^+\) concentration in the irrigation water is 1.9 mM (resulting from the background Na\(^+\) concentrations in both fresh water and fertilizer and fixing the K\(^+\) concentration at point #0 at 6.6 mM). The Na\(^+\) leaching from the substrate was determined by measuring the Na\(^+\) concentration at point #1, and found to be 13.5 mM, resulting in a concentration increase (L) of: 13.5(1-0.63)-1.9=3.1 mM. Even though over time the Na\(^+\) is washed out the substrate, the present study assumes a constant degree of leaching during the consecutive cycles of operation.

The membrane unit needs to remove Na\(^+\) to meet a (steady-state) Na\(^+\) concentration level in the irrigation water <20 mM, i.e., the upper tolerance level for Na\(^+\) of tomato cultivation. **Noteworthy, the model assumes that the membrane unit does not remove any water. The reason is that the LSM under development is composed of a hydrophobic support impregnated with a hydrophobic solvent containing the Na\(^+\) selective carrier 15-crown-5. Prior to entering this organic phase, ions need to be dehydrated with the free energy (ΔG) of dehydration (>0) is compensated for by the ΔG of ion coordination by the 15-crown-5(<0). The water permeation through such LSM systems is negligible.**

### 2.3 Mass balances

At the start of each new cycle, the addition of fresh water and fertilizer at reference point #0 has to compensate for the total water loss due to evapotranspiration and K\(^+\) losses due to plant uptake and removal by the membrane unit. Together with the recycled fraction entering point #0, the fractions of added fresh water and stock solution...
are adjusted such that the $K^+$ concentration of the irrigation water entering the greenhouse at point #0 is 6.6 mM. Given this fixed value of 6.6 mM, adjustment is possible because the total fraction of fresh water and stock solution at point #0 is known to be 1.0 for the first cycle ($n=1$), and 0.63 for all subsequent cycles ($n>1$). The calculation of all parameters is thus based on the fraction of fertilizer stock solution ($\varepsilon$) added at point #0. For that reason, we designated $\varepsilon$ the master variable in our simulations. On the same token, $K^+$ is the master ionic species, dictating, by means of $\varepsilon$, the concentration of the slave ionic species $Na^+$ at point #0 at the start of each new cycle. Once $\varepsilon$ has been calculated from the mass (or volumetric flow) balance at point #0, the $Na^+$ concentration can be calculated as well.

For the very first water cycle, only stock solution and fresh water will meet at point #0. From the second cycle on, however, recycled drain water will join these two water streams at point #0. For this reason, the calculation of the first and the following cycles should be considered separately.

**Figure 2.** Outline of Fig. 1 complemented with the volumetric flows $\Phi_v(1)$-$\Phi_v(5)$ and the process parameters indicated.
2.3.1 Volumetric flow balance for the first two cycles

2.3.1.1 First irrigation cycle (n=1)

Figure 2 shows the basic outline of Fig. 1 but complemented with all relevant parameters referred to in this study. Table 1 lists all these parameters as well as their numerical value as used in this study.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_v(1)$ Volumetric flow</td>
<td>4 m³/hr</td>
</tr>
<tr>
<td>entering the greenhouse</td>
<td></td>
</tr>
<tr>
<td>$\Psi$ K$^+$ concentration in fresh water</td>
<td>4 μM</td>
</tr>
<tr>
<td>$X$ Na$^+$ concentration in fresh water</td>
<td>112.5 μM</td>
</tr>
<tr>
<td>$N$ K$^+$ concentration in fertilizer stock solution</td>
<td>9.5 mM</td>
</tr>
<tr>
<td>$M$ Na$^+$ concentration in fertilizer stock solution</td>
<td>2.7 mM</td>
</tr>
<tr>
<td>$\xi$ fraction of fresh water</td>
<td>0.36</td>
</tr>
<tr>
<td>added at point #0</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon$ fraction of K$^+$</td>
<td>0-1</td>
</tr>
<tr>
<td>entered greenhouse</td>
<td></td>
</tr>
<tr>
<td>taken up by the crop</td>
<td></td>
</tr>
<tr>
<td>$L$ Na$^+$ concentration increase</td>
<td>3.1 mM</td>
</tr>
<tr>
<td>due to Na$^+$ leaching out from</td>
<td></td>
</tr>
<tr>
<td>the coconut-based substrate</td>
<td></td>
</tr>
<tr>
<td>$\theta$ fraction of $\Phi_v(1)$</td>
<td>0.63</td>
</tr>
<tr>
<td>lost due to evapotranspiration</td>
<td></td>
</tr>
<tr>
<td>$\alpha$ fraction of Na$^+$</td>
<td>0-1</td>
</tr>
<tr>
<td>removed from the drain water</td>
<td></td>
</tr>
<tr>
<td>leaving the greenhouse</td>
<td></td>
</tr>
<tr>
<td>$\beta$ fraction of K$^+$</td>
<td>0-1</td>
</tr>
<tr>
<td>removed from the drain water</td>
<td></td>
</tr>
<tr>
<td>leaving the greenhouse</td>
<td></td>
</tr>
<tr>
<td>$\gamma$ Na$^+$ over K$^+$</td>
<td>$\alpha/\beta$</td>
</tr>
<tr>
<td>permeation selectivity of the</td>
<td></td>
</tr>
<tr>
<td>membrane unit</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Description of the parameters used throughout this study, corresponding to Figs. 1 and 2.

Volumetric flows ($\Phi_v$) are presented as fraction of the flow entering the greenhouse, $\Phi_v(1)$ with $\varepsilon$ the fraction of the stock solution and $\xi$ the fraction of fresh water. Flows $\Phi_v(2)$ and $\Phi_v(3)$ represent the volumetric flow of fresh water and stock solution added at point #0, respectively.
Reference point #0

As mentioned, given the optimal K\(^+\) concentration for tomato and taken into account K\(^+\) uptake and evapotranspiration, the K\(^+\) concentration at point #0 is set at 6.6 mM. The Na\(^+\) threshold of 20 mM is the maximum acceptable Na\(^+\) level of the IW leaving the greenhouse. Given the Na\(^+\) leaching out the substrate (3.1 mM) and the evapotranspiration (0.67), the 20 mM translates into a Na\(^+\) of the IW entering the greenhouse of 20x0.37-3.1=4.3 mM. Throughout this study the threshold Na\(^+\) level at point #0 of the incoming IW is set at 4 mM.

The volumetric flow balance reads:

\[
\Phi_v(1) = \Phi_v(2) + \Phi_v(3) = \xi_1 \Phi_v(1) + \varepsilon_1 \Phi_v(1)
\]  
(1)

Suppose \(\Psi\) and \(N\) are the K\(^+\) concentration in the fresh water and in the fertilizer stock solution, respectively. Then, according to Eq. 1, the K\(^+\) mass balance equals:

\[
[K^+]_{0,1} = \Psi \times \xi_1 \Phi_v(1) + N \times \varepsilon_1 \Phi_v(1)
\]  
(2)

Because \(\xi_1 + \varepsilon_1 = 1\) and dividing by \(\Phi_v(1)\) renders for the K\(^+\) concentration:

\[
[K^+]_{0,1} = (1 - \varepsilon_1)\Psi + \varepsilon_1 N = \varepsilon_1 (N - \Psi) + \Psi
\]  
(3)

The fraction of stock solution thus is:

\[
\varepsilon_1 = ([K^+]_{0,1} - \Psi) / (N - \Psi)
\]  
(4)

With \([K^+]_{0,1} = 6.6 \text{ mM}\) and \(\Psi\) and \(N\) being known, the value of \(\varepsilon_1\) is defined.

Once \(\varepsilon_1\) is known, the Na\(^+\) concentration for the first cycle can be calculated by:

\[
[Na^+]_{0,1} = \xi_1 X + \varepsilon_1 M = \varepsilon_1 (M - X) + X
\]  
(5)
where $M$ and $X$ are the Na$^+$ concentration of the stock solution and fresh water, respectively.

Compared to the K$^+$ concentration at point #0, the K$^+$ concentration at point #1 will be different due to K$^+$ uptake by the plants and evapotranspiration. Because $[\text{K}^+]_{0,n}$ is fixed at 6.6 mM, $[\text{K}^+]_{1,n}$ is directly proportional to $[\text{K}^+]_{0,n}$. Let $\mu$ be the fraction of K$^+$ taken up by the plants and $\theta$ the fraction of water loss due to evapotranspiration. Then, $[\text{K}^+]_{1,1}$ is given by:

$$[\text{K}^+]_{1,1} = \frac{(1 - \mu)[\text{K}^+]_{0,1}}{(1 - \theta)}$$  \hspace{1cm} (6)

The Na$^+$ concentration will also change, firstly, because of evapotranspiration, secondly because of the Na$^+$ that leaches out of the coconut-based substrate used, causing an increase of the Na$^+$ concentration, represented by $L$. Then $[\text{Na}^+]_{1,1}$ is given by:

$$[\text{Na}^+]_{1,1} = \frac{([\text{Na}^+]_{0,1} + L)}{(1 - \theta)}$$  \hspace{1cm} (7)

**Reference point #2**

Reference point #2 is located downstream the membrane unit (permeate side) and calculation of the K$^+$ and Na$^+$ concentration at this point therefore requires implementation of the membrane characteristics. Let $\alpha$ be the fraction of Na$^+$ (compared to reference point #1) that permeates the membrane (and with that removed from the system) and $\beta$ the fraction of K$^+$ that permeates the membrane (also removed from the system). Then the K$^+$ and Na$^+$ concentrations are given by $[\text{K}^+]_{2,1} = (1 - \theta)[\text{K}^+]_{1,1}$ and $[\text{Na}^+]_{2,1} = (1 - \alpha)[\text{Na}^+]_{1,1}$, respectively.
2.3.1.2 Second irrigation cycle (n=2)

The calculations for the second cycle are essentially the same as those for the first cycle. The main difference concerns the starting point, i.e., the volumetric flow balance at point #0, now given by:

\[ \Phi_v(1) = \Phi_v(2) + \Phi_v(3) + \Phi_v(5) \]  

Expressed in terms of \( \Phi_v(1) \), Eq. 8 equals:

\[ \Phi_v(1) = \xi_2 \Phi_v(1) + \varepsilon_2 \Phi_v(1) + (1 - \Theta) \Phi_v(1) \]  

Given \( \xi_2 + \varepsilon_2 + (1 - \Theta) = 1 \) and therefore \( \xi_2 = \Theta - \varepsilon_2 \), Eq. 9 reads:

\[ \phi(v, 1) = (\Theta - \varepsilon_2) \phi(v, 1) + \varepsilon_2 \phi(v, 1) + (1 - \Theta)(v, 1) \]  

In analogy with Eq. 2, Eq. 10 results in a \( K^+ \) concentration and \( \varepsilon_2 \) at point #0 of:

\[ [K^+]_{0,2} = \xi_2 \Psi + \varepsilon_2 N + (1 - \Theta) [K^+]_{2,1} = (\Theta - \varepsilon_2) \Psi + \varepsilon_2 N + (1 - \Theta) [K^+]_{2,1} \]  

\[ \varepsilon_2 = ([K^+]_{0,2} - (1 - \Theta) [K^+]_{2,1} - \Theta \Psi) / (N - \Psi) \]  

Once \( \varepsilon_2 \) has been determined, \([Na^+]\) at each point can be calculated:

\[ [Na^+]_{0,2} = \varepsilon_2 (M - X) + \Theta X + (1 - \Theta) [Na^+]_{2,1} \]  

\[ [Na^+]_{1,2} = \frac{[\varepsilon_2 (M - X) + \Theta X] + L}{1 - \Theta} + [Na^+]_{2,1} \]  

\[ [Na^+]_{2,2} = \frac{(1 - \alpha)}{(1 - \Theta)} [\varepsilon_2 (M - X) + \Theta X + L] + (1 - \alpha) [Na^+]_{2,1} \]  

Apart from the fact that \([K^+]_{0,n}\) remains constant for \( n > 1 \) (6.6 mM), \([K^+]_{1,n}\) and \([K^+]_{2,n}\) are constant as well having (if assuming \( \theta = 0.1 \)) a value of 11.4 and 10.3 mM, respectively. In addition, from the second cycle onwards \( \varepsilon_n \) remains constant as well and independent of
This can be seen after, first, substituting $\varepsilon_1$ into $[K^+]_{2,1}$ followed by substituting $[K^+]_{2,1}$ into $\varepsilon_2$, resulting in:

$$\varepsilon_n = \frac{[K^+]_{0,n}(1-(1-\beta)(1-\mu))-\theta \times \Psi}{N-\Psi}$$  \hspace{1cm} (16)

According to the parameter values in Table 1, $\varepsilon_n$ adopts a numerical value expressed in terms of $\beta$ of $0.25 + 0.44\beta$ ($=0.29$ for $\beta=0.1$).

**2.3.3 Generalized expressions**

As evident from Eqs. 3-5, for the first cycle $\varepsilon$ and by implication the $[K^+]$ and $[Na^+]$ as well can all be expressed exclusively in terms of the known process parameters $[K^+]_{0,1}$, $\alpha$, $\beta$, $\mu$, $\theta$, $r$, $N$, $M$, $X$ and $\Psi$. The same is actually true for the second cycle. This can readily be seen after substituting the expression for $[Na^+]_{2,1}$ into Eqs. 13, 14 and 15. Because of this, generalized expressions can be derived for $[Na^+]$ at each reference point as function of known process parameters and the cycle number $n$. The advantage of these generalized expressions is that they allow the direct calculation of $[Na^+]$ during the $n^{th}$ cycle at each reference point without the need to know (calculate) the concentrations during the previous cycles. As an example but also because Figs. 3 and 4 were constructed using these expressions, the generalized expression for $[Na^+]_{0,n}$ and $[Na^+]_{1,n}$ from the 2$^{nd}$ cycle on are given below (for their derivation, see Supplementary Information).

$$[Na^+]_{0,n} = (M - X) \sum_{i=1}^{n-1} [\varepsilon_i \times (1 - \alpha)^{n-i}] + (X\theta + L) \sum_{i=1}^{n-2} [(1 - \alpha)^i] + (X + L)(1 - \alpha)^{(n-1)} + X\theta$$  \hspace{1cm} (17)

$$[Na^+]_{1,n} = \frac{1}{(1-\theta)} \sum_{i=1}^{n} [\varepsilon_i \times (1 - \alpha)^{n-i}] + [(X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^{(i-1)}] + (1 - \alpha)^{(n-2)} \times (X + L)]$$  \hspace{1cm} (18)
Note that for \( n=2 \) and after a number of repeated substitutions, Eqs. 17 and 18 reduce to Eqs. 13 and 14, respectively.

4. Results and discussion

4.1 Membrane selectivity

The Na\(^+\) over K\(^+\) permeation selectivity also is an intrinsic membrane property. As stated previously, one of our prime goals is to determine the minimum membrane selectivity (\( \gamma \)) required to maintain the Na\(^+\) concentration in the IW below the upper tolerance level of 4-5 mM. Because the membrane selectivity (\( \gamma \)) is defined as the ratio of its permeability towards Na\(^+\) (\( \alpha \)) and its permeability towards K\(^+\) (\( \beta \)), the permeation of both ion species is coupled. With both \( \beta \) and \( \gamma \) set at a fixed value, \( \alpha \) can be calculated and with that the Na\(^+\) level at point #2, which, in turn, allows the calculation of the Na\(^+\) level at point #0 at the start of a new cycle.

To compromise between minimizing K\(^+\) loss and dealing with a finite membrane selectivity, the value of \( \beta \) is set (arbitrarily) at 0.1, implying that 10% of K\(^+\) is removed together with Na\(^+\). In combination with a membrane that does not discriminate between K\(^+\) and Na\(^+\) (\( \gamma = 1 \)) this results in a Na\(^+\) removal of also 10%. In this case it is expected to see a dramatic Na\(^+\) accumulation in the IW. Figure 3 confirms this expectation showing the Na\(^+\) level in the IW after 10 cycles of operation and for a Na\(^+\) over K\(^+\) selectivity ranging from \( \gamma = 1 \) to 9. Note that \( \gamma = 1 \) indeed results in staggering Na\(^+\) concentrations after 10 cycles of operation.
Figure 3. Accumulation of Na\(^+\) in the irrigation water entering the greenhouse (i.e., at point #0) after 10 cycles of operation for a membrane with a Na\(^+\)/K\(^+\) selectivity ranging from 1 to 9 and a K\(^+\) permeability \(\beta\) of 0.1, i.e., with 10\% - 90\% of the Na\(^+\) and 10\% of the K\(^+\) removed.

Figure 4 explores the relationship between membrane selectivity and the Na\(^+\) level at points #0 and #1 during 15 subsequent cycles of operation, given the 10\% removal of K\(^+\) (\(\beta = 0.1\)) and for a Na\(^+\) over K\(^+\) membrane permeability selectivity ranging from 5 to 9. A membrane selectivity of 5 does not suffice to achieve a steady-state [Na\(^+\)] below the threshold of 4 mM at point #0 (A) and of 20 mM at point #1 (B). Indeed, it requires at least a selectivity of 6 to accomplish steady-state levels remaining below these thresholds. As indicated in Fig. 2, Na\(^+\) is entering the system from three sources, the fresh water, the fertilizer content and the Na\(^+\) leaching from the coconut-based substrate used. As already remarked, from the second cycle on \(\varepsilon\) adopts a constant numerical value of 0.25 + 0.44\(\beta\), i.e., 0.29 for \(\beta = 0.1\). Given \(\theta = 0.63\), \(\xi\) equals 0.34, implying that the amount of Na\(^+\) entering the system from the fresh water and fertilizer is 3 and 72 g/hr,
respectively. The Na⁺ concentration increase due to leaching equals 3.1 mM, resulting in 285 g/hr. Evidently, at steady state the total amount of 360 gr/hr equals the amount of Na⁺ that needs to be removed by the membrane unit.
Figure 4. (A). [Na⁺] in the irrigation water entering the greenhouse at point #0; (B). [Na⁺] in the irrigation water leaving the greenhouse at point #1 during 15 cycles of operation, for a Na⁺/K⁺ membrane selectivity ranging from 5 to 9 and a K⁺ permeability β of 0.1, i.e., with 50% - 90% of the Na⁺ and 10% of the K⁺ removed. Dotted lines represent the threshold of 4 mM of the Na⁺ content of the IW entering the greenhouse (A) and the physiological tolerance threshold for tomato of 20 mM (B).
In order to maintain a steady-state K+ concentration in the IW of 6.6 mM, the added amount of K+, originating from the fertilizer, equals $\varepsilon_n \times N \times \Phi_v(1) = 430 \text{ g/hr}$.

### 4.3 Implementation

As argued in the previous paragraph, Na+ leaching from the substrate contributes most to the amount of Na+ entering the IW system, even if considering that over time this amount reduces. So even if the Na+ content of the fertilizer could be drastically reduced, Na+ still accumulates in the (recycled) IW but at a lower rate.

We envisage implementing the membrane-to-be-developed in an electro dialysis (ED)-like setting, operating under constant current conditions. From the viewpoint of capital costs, a key parameter is the total required membrane surface area ($A$), given the amount of Na+ that need to be removed. Eq. 19 gives the value of $A$ as a function of volumetric flow through the membrane module $Q$, the Faraday constant $F$ (96485 C/mol), the Na+ concentration difference between the water entering and leaving the membrane module, the current density ($i$) and the current utilization factor ($f$) [22]:

$$A = Q \times F \times ([\text{Na}^+]_{1,2} - [\text{Na}^+]_{2,2}) / if$$  \hspace{1cm} (19)

The volumetric flow $Q$ equals $\Phi_v(4) = 0.37 \times \Phi_p(1) = 4.1 \times 10^{-4} \text{ m}^3/\text{s}$. As mentioned before, any water flow arising from either osmosis or electro osmosis is ignored, given the strong hydrophobic nature of the LSM system. According to Fig. 2 and given $\alpha=0.6$ and $\beta=0.1$ (Fig. 4A with $\gamma=6$), $[\text{Na}^+]_{0,n}$ reaches a steady-state value of 3.45 mM. The difference between the Na+ concentration of the solution entering and leaving the membrane then is $0.6\times(3.5+3.1)/0.37=10.7$ mM. Note that this concentration difference results in $10.7 \times 10^{-3} \times 23 \times 4000 \times 0.37 = 365 \text{ gr Na+/hr}$ that needs to be removed, essentially the same amount as previously derived from the amount of Na+ entering the system.
for the current density, we take a ‘typical’ value for ion exchange membranes given a
total ionic strength of the incoming water of around 25-30 mM, i.e., 10 A/m² [23].
Further, as a rather conservative estimate the current utilization factor \( f \) is assumed to
be 0.6, implying that 60% of the current is actually carried by \( \text{Na}^+ \), the remaining 40% by
\( \text{K}^+ \) and other ion species present. Substituting these numbers in Eq. 19 renders a
membrane surface area of 70 m². In practice, this could be achieved by constructing ED
stacks with a number of cells in series. For instance, three ED modules, each comprising
of a stack of 12 cells with a membrane surface area of 2 m² each.
So far our analysis has been based on average parameter values over one entire year,
thereby ignoring seasonal variations. In any real-life application, the level of
evapotranspiration and nutrient uptake will depend on time of the year and crop growth.
This asks for a dynamic rather than static nutrient control. One option could be to
monitor the water conductivity at point #1 and use this signal as input parameter for the
electro dialysis unit. This way, the recorded conductivity (as measure of the \( \text{Na}^+ \) content)
allows fine tuning of the constant current magnitude applied during operation, and with
that the amount of \( \text{Na}^+ \) (and \( \text{K}^+ \)) removed per unit time. Evidently, the implication of
such dynamic control is that \( \varepsilon_n \) requires re-adjustment as well.

4.3 Economics perspective
The specifications of the membrane-to-be developed, e.g. regarding membrane thickness
and the required density of the crown ethers (as carrier molecules) in the membrane,
remain elusive and await further study (in progress). Nevertheless, despite these
uncertainties a few general remarks can be put forward.
Firstly, the capital cost of the LSM currently developed and validated is to a large extent
dominated by the amount of 15-crown-5 needed. When purchased from TCI-Chemicals
and given the 15-crown-5 density (0.2 M), the membrane thickness (100 μm) and a support porosity of 50% the estimated cost price amounts to 78 euro per m². To put this number in perspective, the price of typical commercially available ion exchange membranes is around 30 euro per m². The most promising options to bring the price from the LSM down, seem a thinner membrane and upscaling 15-crown-5 (in-house) synthesis. It should be mentioned however that the (at this moment unknown and therefore not considered here) manufacturing cost contribute significantly to if not dominate the cost prize (Fuji Film, Netherlands; personal communication).

Secondly, the operational costs on the other hand will be dominated by the power needed to run the system. Based on the specifications of a typical ED system and given the salt concentration in the feed, the power consumption will be in the range 0.7 – 2.5 kWh/m³ [24]. The power consumption is linear with the applied current density [22] and as evident from Eq. 19, there are essentially three ways to reduce the required total membrane surface area: by reducing the volumetric flow through the system, by increasing the current utilization factor or by increasing the current density. Reduction of the volumetric flow could (possibly) be accomplished by a different configuration altogether. For instance, by positioning the membrane module not in the main stream (as in Figs. 1, 2) but instead in a bypass. This option will be explored in more detail once we (experimentally) obtained the actual specifications of our membrane under development. Improving the current utilization factor implies a higher Na⁺ over K⁺ membrane selectivity. Even though the cost for re-supplementing the IW with K⁺ will go down, the membrane itself will (probably) be more expensive due to the higher density of crown ethers required. Finally, a higher current density will reduce the total membrane surface area needed but increase the power needed during operation. As pointed out by Strathmann [22], the opposite effect of current density on required...
membra ne surface area and energy cost may translate in an optimal current density, resulting in the lowest overall costs.

Apart from the foregoing discussion and as remarked earlier on, the prime incentive for the current analysis was inspired more by environmental issues than by economics, even though at a certain point both types of arguments might become intertwined. For instance, (European) legislation becomes more stringent and might even aim for zero discharge in 2027, with discharge allowed only at high(er) cost [25, 26]. For now, it remains speculative how including such discharge cost will affect the overall balance.

5. Conclusion

Excess Na\(^+\) in irrigation water needs to be removed to a level dictated by the tolerance threshold specific for the particular crop, for tomato 20 mM. The closed-loop irrigation water system described here includes a membrane-based module to remove excess Na\(^+\) while preserving the (nutrient) K\(^+\) as much as possible. Based on real-life process parameters, the present study indicates that a Na\(^+\) over K\(^+\) membrane permeation selectivity of 6 already suffices to remain the Na\(^+\) level the plants are exposed to below 20 mM, at least if accepted that 10% of the K\(^+\) is removed as well. If implemented in an electro dialysis set-up while assuming a constant current density of 10 A/m\(^2\), the estimated total membrane surface is 70 m\(^2\). Considering the opposite effect of current density on required membrane surface area and energy cost, an optimum current density is hypothesized, resulting in a minimum of overall cost.

Conflict of Interest Statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.
Acknowledgements

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References

Supporting information

Supporting information for “Modelling the Selective Removal of Sodium Ions from Greenhouse Irrigation Water Using Membrane Technology”

Z. Qian a,c, H. Miedema c, L.C.P.M. de Smet b, c, E.J.R. Sudhöltzer a

As in the manuscript, the nomenclature practiced is based on the use of two indices, the first representing the reference point, the second the cycle number. For instance, \([\text{Na}^+]_{2,3}\) refers to the Na\(^+\) concentration at point #2 during the third cycle.

The manuscript gives the equations for \(\epsilon\) and the \(K^+\) and Na\(^+\) concentrations during the 1\(^{st}\) and 2\(^{nd}\) cycle of operation. Here the expressions for the Na\(^+\) concentrations at the three reference points during the 2\(^{nd}\) cycle are given again but, in contrast to the manuscript, this time exclusively in terms of known parameters, as required to derive the generalized expressions.

\begin{align}
[\text{Na}^+]_{0,2} &= (M - X)[\epsilon_2 + \epsilon_1 (1 - \alpha)] + (X + L)(1 - \alpha) + \Theta X \\
(1) \\
[\text{Na}^+]_{1,2} &= [(M - X)[\epsilon_2 + \epsilon_1 (1 - \alpha)] + (X + L)(1 - \alpha) + \Theta X + L]/(1 - \theta) \\
(2) \\
[\text{Na}^+]_{2,2} &= \\
&= [(M - X)[\epsilon_2 (1 - \alpha) + \epsilon_1 (1 - \alpha)^2] + (X + L)(1 - \alpha)^2 + (\Theta X + L)(1 - \alpha)]/ (1 - \theta) \\
(3)
\end{align}

As shown in the manuscript (Eq. 16), from the 2\(^{nd}\) cycle on \(\epsilon_n\) becomes constant:

\[\epsilon_n = \frac{[K^+]_{0,n}(1 - (1 - \beta)(1 - \mu)) - \theta \times \Psi}{N - \Psi} (4)\]

Apart from the fact that \([K^+]_{0,n}\) remains constant for \(n>1\) (6.6 mM), \([K^+]_{1,n}\) and \([K^+]_{2,n}\) are constant as well having (if assuming \(\theta=0.1\)) a value of 11.4 and 10.3 mM, respectively.

For this reason, this Supplement is restricted to the Na\(^+\) level at each reference point for \(n>2\).

**Mass Balance for the third irrigation cycle (n=3)**

**Reference point #0**
In analogy with Eq. 13 in the manuscript, once $\varepsilon_3$ is known, $[\text{Na}^+]_{0,3}$ is given by:

$$[\text{Na}^+]_{0,3} = \varepsilon_3 (M - X) + \varepsilon_2 (M - X) (1 - \alpha) + \varepsilon_1 (M - X) (1 - \alpha)^2 + (X + L) (1 - \alpha)^2 + (X\theta + L) (1 - \alpha) + X\theta$$

(5)

**Reference point #1**

Likewise, in analogy with Eq. 14 in the manuscript, $[\text{Na}^+]_{1,3}$ reads:

$$[\text{Na}^+]_{1,3} = [(M - X) \times [\varepsilon_3 + \varepsilon_2 (1 - \alpha) + \varepsilon_1 (1 - \alpha)^2]] + (1 - \alpha)^2 (X + L) + (1 - \alpha) \times (X\theta + L) + X\theta + L] / (1 - \theta)$$

(6)

**Reference point #2**

In analogy with $[\text{Na}^+]_{2,1} = (1 - \alpha)[\text{Na}^+]_{1,1}$, the $[\text{Na}^+]_{2,3}$ reads:

$$[\text{Na}^+]_{2,3} = [(M - X) \times [\varepsilon_3 (1 - \alpha) + \varepsilon_2 (1 - \alpha)^2 + \varepsilon_1 (1 - \alpha)^3]] + (1 - \alpha)^3 (X + L) + (1 - \alpha)^2 (X\theta + L) + (1 - \alpha) (X\theta + L) + X\theta + L] / (1 - \theta)$$

(7)

**Mass Balance for the fourth irrigation cycle (n=4)**

**Reference point #0**

$$[\text{Na}^+]_{0,4} = (M - X) \times [\varepsilon_4 + \varepsilon_3 (1 - \alpha) + \varepsilon_2 (1 - \alpha)^2 + \varepsilon_1 (1 - \alpha)^3)] + (1 - \alpha)^3 (X + L) + (1 - \alpha)^2 (X\theta + L) + (1 - \alpha) (X\theta + L) + X\theta$$

(8)

**Reference point #1**

$$[\text{Na}^+]_{1,4} = [(M - X) \times [\varepsilon_4 + \varepsilon_3 (1 - \alpha) + \varepsilon_2 (1 - \alpha)^2 + \varepsilon_1 (1 - \alpha)^3]] + (1 - \alpha)^3 (X + L) + (1 - \alpha)^2 (X\theta + L) + (1 - \alpha) (X\theta + L) + X\theta + L] / (1 - \theta)$$

(9)

**Reference point #2**

$$[\text{Na}^+]_{2,4} = [(M - X) \times [\varepsilon_4 (1 - \alpha) + \varepsilon_3 (1 - \alpha)^2 + \varepsilon_2 (1 - \alpha)^3 + \varepsilon_1 (1 - \alpha)^4] + (1 - \alpha)^4 \times (X + L) + (1 - \alpha)^3 (X\theta + L) + (1 - \alpha)^2 (X\theta + L) + (1 - \alpha) (X\theta + L)] / (1 - \theta)$$

(10)
Mass Balance for the fifth irrigation cycle (n=5)

**Reference point #0**

\[
[Na^+]_{0,5} = (M - X) \times [\varepsilon_5 + \varepsilon_4(1 - \alpha) + \varepsilon_3(1 - \alpha)^2 + \varepsilon_2(1 - \alpha)^3 + \varepsilon_1(1 - \alpha)^4] + \\
(1 - \alpha)^4(X + L) + (1 - \alpha)^3(1 - \alpha)(X\theta + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta
\]  

(11)

**Reference point #1**

\[
[Na^+]_{1,5} = [(M - X) \times [\varepsilon_5 + \varepsilon_4(1 - \alpha) + \varepsilon_3(1 - \alpha)^2 + \varepsilon_2(1 - \alpha)^3 + \varepsilon_1(1 - \alpha)^4]] + \\
(1 - \alpha)^5(X + L) + (1 - \alpha)^4(1 - \alpha)(X\theta + L) + (1 - \alpha)^3(1 - \alpha)(X\theta + L) + \\
(1 - \alpha)^2(1 - \alpha)(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta + L]/(1 - \theta)
\]  

(12)

**Reference point #2**

\[
[Na^+]_{2,5} = [(M - X) \times [\varepsilon_5 (1 - \alpha) + \varepsilon_4 (1 - \alpha)^2 + \varepsilon_3 (1 - \alpha)^3 + \varepsilon_2 (1 - \alpha)^4 + \\
\varepsilon_1 (1 - \alpha)^5]] + (1 - \alpha)^5(X + L) + (1 - \alpha)^4(1 - \alpha)(X\theta + L) + (1 - \alpha)^3(1 - \alpha)(X\theta + L) + \\
(1 - \alpha)^2(1 - \alpha)(X\theta + L) + (1 - \alpha)(X\theta + L)]/(1 - \theta)
\]  

(13)

**Generalized expressions for the n\textsuperscript{th} irrigation cycle (n≥2)**

When comparing Eqs. 1, 5, 8 and 11, the resemblance in the form of the expressions becomes evident. This resemblance allows the formulation of a generalized expression for [Na\textsuperscript{+}]\textsubscript{0,n} as function of n:

\[
[Na^+]_{0,n} = (M - X) \sum_{i=1}^{n} [\varepsilon_i \times (1 - \alpha)^{n-i}] + (X\theta + L) \sum_{i=1}^{n-1} [(1 - \alpha)^i] + (X + L) \times \\
(1 - \alpha)^{(n-1)} + X\theta
\]  

(14)
the generalized expression for \([\text{Na}^+]_{1,n}\) is:

\[
[\text{Na}^+]_{1,n} = \frac{1}{(1-\theta)} [(M - X) \sum_{i=1}^{n} [\epsilon_i \times (1 - \alpha)^{n-i}] + [(X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^{(i-1)}] + (1 - \alpha)^{(n-1)} \times (X + L)]
\]

(15)

Finally, using \([\text{Na}^+]_{2,n} = (1 - \alpha)[\text{Na}^+]_{1,n}\), the generalized expression for \([\text{Na}^+]_{2,n}\) becomes:

\[
[\text{Na}^+]_{1,n} = \frac{1}{(1-\theta)} [(M - X) \sum_{i=1}^{n} [\epsilon_i \times (1 - \alpha)^{n-i+1}] + [(X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^{i}] + (1 - \alpha)^{n} \times (X + L)]
\]

(16)
Figure 2

\[ [K^+] = N = 9.5 \text{mmol/l} \]
\[ [Na^+] = M = 2.7 \text{mmol/l} \]

\[ \Phi_2 = \xi \Phi_1 \]
\[ \Phi_3 = \epsilon \Phi_1 \]
\[ \Phi_4 = (1-\theta) \Phi_1 \]
\[ \Phi_5 = \Phi_4 \]

Stock Solution

\[ [K^+]_{0,n} = 6.6 \text{ mM} \]
\[ [Na^+]_{0,n} \leq 4 \text{ mM} \]

Greenhouse

\[ [K^+]_{1,n} = (1-\mu)[K^+]_{0,n}/(1-\theta) \]
\[ [Na^+]_{1,n} = ([Na^+]_{0,n}+L)/(1-\theta) \]

Membrane System

\[ [K^+]_{2,n} = (1-\beta)[K^+]_{1,n} \]
\[ [Na^+]_{2,n} = (1-\alpha)[Na^+]_{1,n} \]

Stripped Na^+
Figure 3

Membrane $[\text{Na}^+] / [\text{K}^+]$ selectivity $\Upsilon$ vs. $[\text{Na}^+] (\text{mmol/l})$
Figure 4

(A) [Na\(^+\)] (mmol/l) vs. Cycle number

(B) [Na\(^+\)] (mmol/l) vs. Cycle number
<table>
<thead>
<tr>
<th>Variables</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_v(1)$</td>
<td>Volumetric flow entering the greenhouse</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>$K^+$ concentration in fresh water</td>
</tr>
<tr>
<td>$X$</td>
<td>Na$^+$ concentration in fresh water</td>
</tr>
<tr>
<td>$N$</td>
<td>$K^+$ concentration in fertilizer stock solution</td>
</tr>
<tr>
<td>$M$</td>
<td>Na$^+$ concentration in fertilizer stock solution</td>
</tr>
<tr>
<td>$\xi$</td>
<td>fraction of fresh water added at point #0</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>fraction of fertilizer stock solution added at point #0</td>
</tr>
<tr>
<td>$\mu$</td>
<td>fraction of $K^+$ entering the greenhouse taken up by the crop</td>
</tr>
<tr>
<td>$L$</td>
<td>Na$^+$ concentration increase due to Na$^+$ leaching out from the coconut-based substrate</td>
</tr>
<tr>
<td>$\theta$</td>
<td>fraction of $\Phi_v(1)$ lost due to evapotranspiration</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>fraction of Na$^+$ removed from the drain water leaving the greenhouse</td>
</tr>
<tr>
<td>$\beta$</td>
<td>fraction of $K^+$ removed from the drain water leaving the greenhouse</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Na$^+$ over $K^+$ permeation selectivity of the membrane unit</td>
</tr>
</tbody>
</table>

**Table 1.** Description of the parameters used throughout this study, corresponding to Figs. 1 and 2.