

## Modelling the selective removal of sodium ions from greenhouse irrigation water using membrane technology

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Title: Modelling the Selective Removal of Sodium Ions from Greenhouse  
Irrigation Water Using Membrane Technology

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Modelling; Na<sup>+</sup> over K<sup>+</sup> membrane selectivity

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Abstract: A model is presented for the Na<sup>+</sup> and K<sup>+</sup> 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<sup>+</sup> but includes a membrane unit for the selective removal of Na<sup>+</sup> as well. As determined by the membrane properties, some of the K<sup>+</sup> is removed as well. Based on real-life process parameters, the model calculates the Na<sup>+</sup> and K<sup>+</sup> concentration at three reference points. These process parameters include the evapotranspiration rate, the K<sup>+</sup> uptake by the plants, the Na<sup>+</sup> and K<sup>+</sup> content of the fertilizer, the Na<sup>+</sup> leaching out from the hydroponic substrate material, and the Na<sup>+</sup> and K<sup>+</sup> removal efficiency of the membrane unit. Using these parameters and given a constant K<sup>+</sup> concentration of the irrigation water entering the greenhouse of 6.6 mM (resulting in the optimal K<sup>+</sup> 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<sup>+</sup> over K<sup>+</sup> selectivity of 6, after a number of cycles the Na<sup>+</sup> 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<sup>+</sup> 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,

Zexin Qian

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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<sup>+</sup> and K<sup>+</sup> 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 greenhous. 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<sup>+</sup> entry. We added a calculation of the amount of Na<sup>+</sup> 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<sup>+</sup> entering the IW system. So even if the Na<sup>+</sup> content of the fertilizer could be drastically reduced, Na<sup>+</sup> 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<sup>+</sup> 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<sup>+</sup> is a key to separate it from smaller Na<sup>+</sup>. 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<sup>+</sup> 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<sup>+</sup>, K<sup>+</sup> 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<sup>+</sup> 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  $\gg 1$ , 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 173 – 178).*

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 m<sup>3</sup> 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 355 – 378 and 403 – 421.*

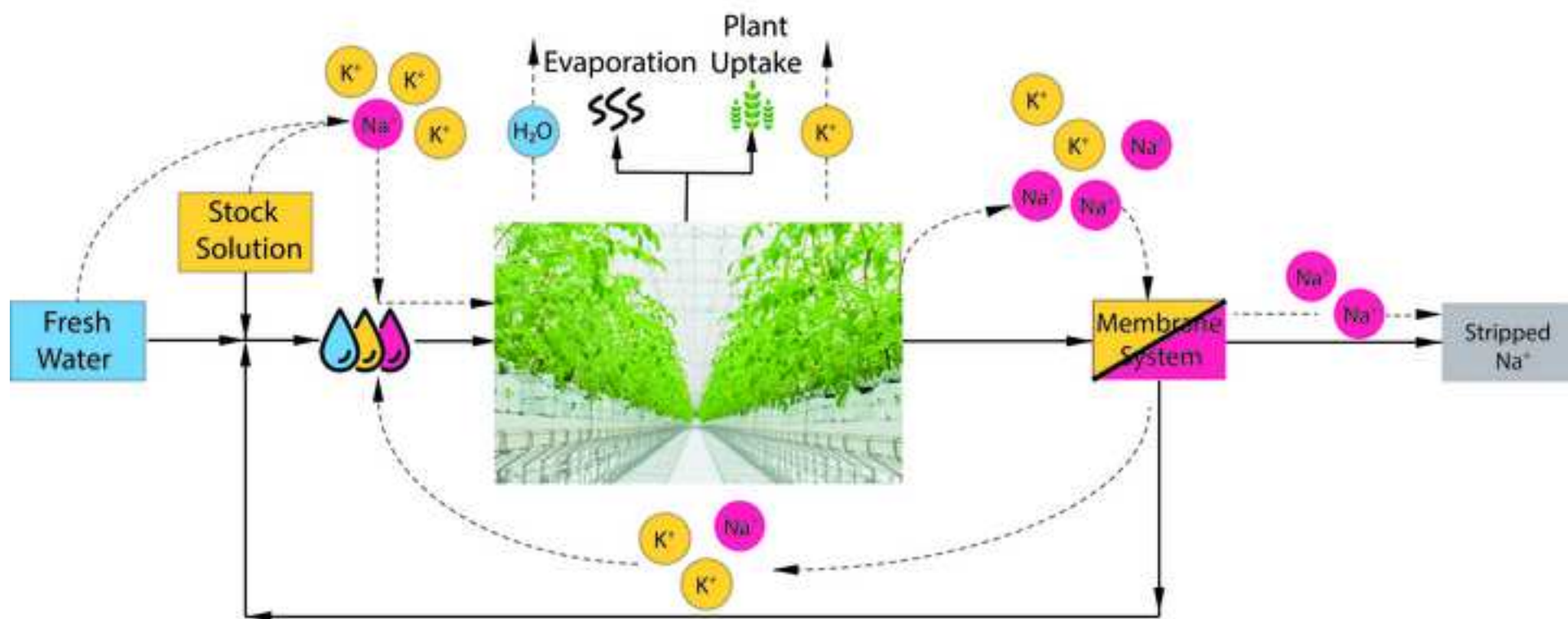
19. line 432: note that the final decision for use or not is dictated by profit margins. Minimising costs is not enough; profit is needed. Or do you mean that subsidies may be used to turn a cost into a profit?

*>>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<sup>+</sup> content, should be considered too.

*>>As argued, the Na<sup>+</sup> concentration increase due to leaching equals 285 g/hr, far more than the Na<sup>+</sup> 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.*





## \*Research Highlights

- Simulation of Na<sup>+</sup> and K<sup>+</sup> concentration in recycled closed-loop irrigation water.
- Development of a membrane-based system for the removal of excess Na<sup>+</sup>.
- Permeation selectivity of 6 suffices to maintain the system under Na<sup>+</sup> threshold.
- Implementation of an electro-dialysis like set-up.
- Required membrane surface area around 70 m<sup>2</sup>.

# 1 **Modelling the Selective Removal of Sodium Ions from** 2 **Greenhouse Irrigation Water Using Membrane Technology**

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## 11 **Abstract**

12 A model is presented for the Na<sup>+</sup> and K<sup>+</sup> levels in the irrigation water of greenhouses,  
13 specifically those for the cultivation of tomato. The model, essentially based on mass  
14 balances, not only describes the accumulation of Na<sup>+</sup> but includes a membrane unit for  
15 the selective removal of Na<sup>+</sup> as well. As determined by the membrane properties, some  
16 of the K<sup>+</sup> is removed as well. Based on real-life process parameters, the model calculates  
17 the Na<sup>+</sup> and K<sup>+</sup> concentration at three reference points. These process parameters  
18 include the evapotranspiration rate, the K<sup>+</sup> uptake by the plants, the Na<sup>+</sup> and K<sup>+</sup> content  
19 of the fertilizer, the Na<sup>+</sup> leaching out from the hydroponic substrate material, and the  
20 Na<sup>+</sup> and K<sup>+</sup> removal efficiency of the membrane unit. Using these parameters and given a  
21 constant K<sup>+</sup> concentration of the irrigation water entering the greenhouse of 6.6 mM  
22 (resulting in the optimal K<sup>+</sup> concentration for tomato cultivation), the composition of the  
23 solution is completely defined at all three reference points per irrigation cycle. Prime  
24 aim of this investigation is to explore the requirements for the selective membrane that

25 currently is developed in our lab. It is found that even for a limited  $\text{Na}^+$  over  $\text{K}^+$   
26 selectivity of 6, after a number of cycles the  $\text{Na}^+$  level reaches steady state at a level  
27 below the upper (toxic) threshold for tomato cultivation (20 mM). Economic aspects and  
28 ways of implementation of such a system are briefly discussed.

## 29 **Keywords**

30 Greenhouse; Irrigation water; Sodium removal; Mass balance; Modelling;  $\text{Na}^+$  over  $\text{K}^+$   
31 membrane selectivity

## 32 **1. Introduction**

33 Closed-loop soilless or hydroponic systems are already widely used if not, at least in  
34 certain countries e.g. The Netherlands, common practice in horticulture[1]. Nutrients  
35 and water are supplied continuously to the irrigation water (IW) to compensate for  
36 nutrient uptake by the plants and water loss due to evapotranspiration. Ideally, the  
37 nutrient and water supply are fine-tuned such that the nutrient concentration and the  
38 osmotic pressure of the drainage solution remain (fairly) constant. Consequently,  
39 nutrients, which are present but are not taken up by the plant, accumulate in the IW.  $\text{Na}^+$   
40 is a typical example of an ion that over time builds up in the IW [2]. High  $\text{Na}^+$  levels  
41 inhibit plant growth directly or indirectly by hampering the uptake of other nutrients [3-  
42 6]. Because of the detrimental effects of high  $\text{Na}^+$ , the IW  $\text{Na}^+$  level has been subject of  
43 numerous studies already [7-9]. These studies are restricted however to simulation  
44 studies, validated or not by monitoring the actual  $\text{Na}^+$  level in the IW during crop growth.  
45 Despite the detrimental effects at higher levels, plants do show a certain tolerance for  
46  $\text{Na}^+$ . Reported  $\text{Na}^+$  threshold values for tomato vary somewhat but levels above 5 dS/m,  
47 equivalent to 50 mM, prove to inhibit growth and yield [10]. The threshold value might

48 depend on the tomato species; the value used in the present study is 20 mM. As soon as  
49  $\text{Na}^+$  exceeds the threshold level, the IW is discharged and needs to be renewed. After  
50 replenishing the system with freshly prepared IW the entire process of  $\text{Na}^+$  building up  
51 starts all over again. Our goal is, apart from monitoring, to develop a (membrane-based)  
52 system that selectively removes accumulated  $\text{Na}^+$  from the IW. A complication arises  
53 from the fact that  $\text{K}^+$ , an essential plant nutrient, has very similar physicochemical  
54 properties as  $\text{Na}^+$ . Both (alkali metal) ion species have the same valence (+1) and are  
55 similar in size with ionic radii of 1.90 and 2.43 Ångstrom for  $\text{Na}^+$  and  $\text{K}^+$ , respectively.  
56 However, a key (physiological) difference between the two ion species is that  $\text{Na}^+$  is  
57 hardly taken up by the plant and is the major cause of salinity toxicity [11, 12]. Excess  
58  $\text{Na}^+$  thus needs to be removed, either by resin-based absorbance technology or  
59 membrane technology. The latter is preferred because it circumvents the necessity of  
60 resin regeneration once it has become saturated with  $\text{Na}^+$ .

61 The fact that  $\text{Na}^+$  and  $\text{K}^+$  behave very much the same because they share similar  
62 physicochemical properties is exactly the reason that there are no commercial  
63 *separation* membranes available yet that discriminate between the two ion species. Here  
64 separation refers to a membrane that allows high fluxes. Selective membranes for ion  
65 selective electrodes (ISE) do exist already. However, ion fluxes over such *potentiometric*  
66 membranes are by definition essentially zero [13, 14]. Ceramic NASICON-based  
67 membranes do selectively transport  $\text{Na}^+$  [15]. However, only harsh operational  
68 conditions like high temperature or high acidity or alkalinity justify their use because of  
69 the high price. In addition, the high conductivity demonstrated in battery applications  
70 remains relatively low compared to the conductivity of typical polymeric ion exchange  
71 membranes [16].

72 To impose selectivity on a polymeric or Liquid Supported Membrane (LSM), a compound  
73 is blended in with the membrane polymer or a mobile carrier is added to the organic  
74 phase of the LSM [17, 18, 19]. Na<sup>+</sup> selective carriers include natural monensin and the  
75 synthetic crown ether 15-crown-5. Monensin has been used for ISE applications as well  
76 as for Na<sup>+</sup> extraction by ionic liquids enriched with monensin [20, 21]. Current focus of  
77 our lab is on developing a LSM-based system with the organic phase supplemented with  
78 15-crown-5.

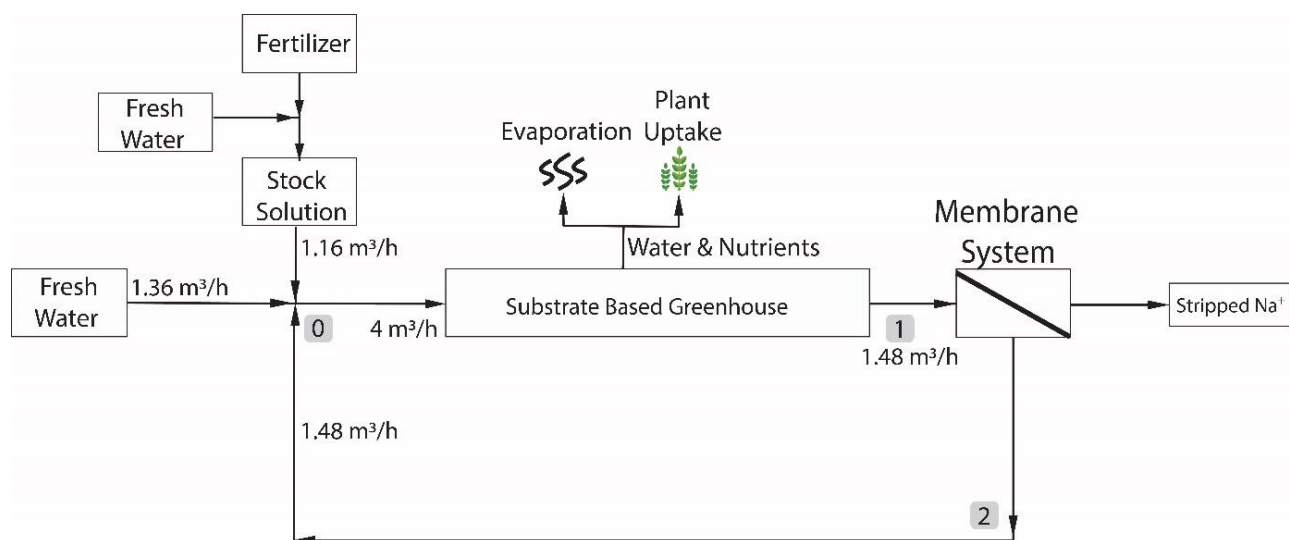
79 The technological challenge thus is to develop a separation membrane that permeates  
80 Na<sup>+</sup> but not, or at least to a much lower extent, K<sup>+</sup>. Obviously, the less permeable for K<sup>+</sup>,  
81 the less K<sup>+</sup> needs to be re-supplied to compensate for this loss. Therefore,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

97 discharge of  $K^+$ . The membrane specifications resulting from the present analysis will  
98 guide us in the currently performed investigation to actually fabricate such a membrane  
99 system.

## 100 **2. Material & Methods**

### 101 **2.1 System & Model Design**

102 The greenhouse recycling system considered in the present study is schematically  
103 shown in Fig. 1. The fresh water source is accumulated rainwater whereas dissolved  
104 fertilizer is added as stock solution with a composition adjusted to the requirement of  
105 the particular greenhouse crop. Also indicated in Fig. 1 is the membrane unit  
106 responsible for  $Na^+$  removal and producing a waste stream of  $Na^+$ . Depending on the  
107 membrane selectivity, this waste stream is to a more or lesser extent contaminated with  
108  $K^+$ . Along the process line, three reference points are distinguished: point #0 where  
109 fresh water, stock solution and recycled drain water are mixed forming fresh (i.e., next  
110 cycle) irrigation water entering the greenhouse; #1 the drain water leaving the  
111 greenhouse before it enters the membrane module and #2 the drain water after  
112 filtration by the membrane unit. The model aims to calculate the  $Na^+$  and  $K^+$   
113 concentrations during each cycle ( $n$ ) at the three reference points indicated. The  
114 nomenclature practiced throughout this study is based on the use of two indices, the  
115 first representing the reference point, the second the cycle number. For instance,  $[K^+]_{2,3}$   
116 refers to the  $K^+$  concentration at reference point #2 during the third cycle.



117

118 **Figure 1.** Outline of a substrate-based greenhouse irrigation water system with the  
 119 drain water recycled and including a membrane unit for the selective removal of Na+.  
 120 Reference points #0-2 are indicated as well as the relevant (steady-state) volumetric  
 121 flows while assuming a K<sup>+</sup> loss of 10% (i.e.,  $\beta=0.1$ ).

122

## 123 2.2 Process parameters

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

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

132 *Fresh water.* Since rainwater is used as fresh water source at reference point #0, three  
 133 sets of samples were collected during September-October-2017 at Wetsus in  
 134 Leeuwarden, the Netherlands. The K<sup>+</sup> and Na<sup>+</sup> levels were analyzed using inductively  
 135 coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 5000  
 136 Series). All required dilutions were carried out with ultrapure water (Millipore



137 purification unit). The average K<sup>+</sup> and Na<sup>+</sup> concentration in rain water was 158 µg/l and  
138 2587 µg/l, resulting in background concentrations of 4 µM and 112.5 µM for K<sup>+</sup> and Na<sup>+</sup>,  
139 respectively.

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

145 *K<sup>+</sup> concentration*. K<sup>+</sup> enters the system from two potential sources:

- 146 1) The background K<sup>+</sup> concentration in fresh water (4 µM), and
- 147 2) The K<sup>+</sup> content of the fertilizer stream (9.5 mM).

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

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

158 *Na<sup>+</sup> concentration*. Na<sup>+</sup> enters the system from three potential sources:

- 159 1) The background Na<sup>+</sup> concentration in fresh water (112.5 µM),

160 2) The Na<sup>+</sup> content of the fertilizer (2.7 mM), and  
161 3) The Na<sup>+</sup> leaching from the (coconut-based) substrate material used in the greenhouse,  
162 leads to a Na<sup>+</sup> enrichment of the irrigation water (*vide infra*).

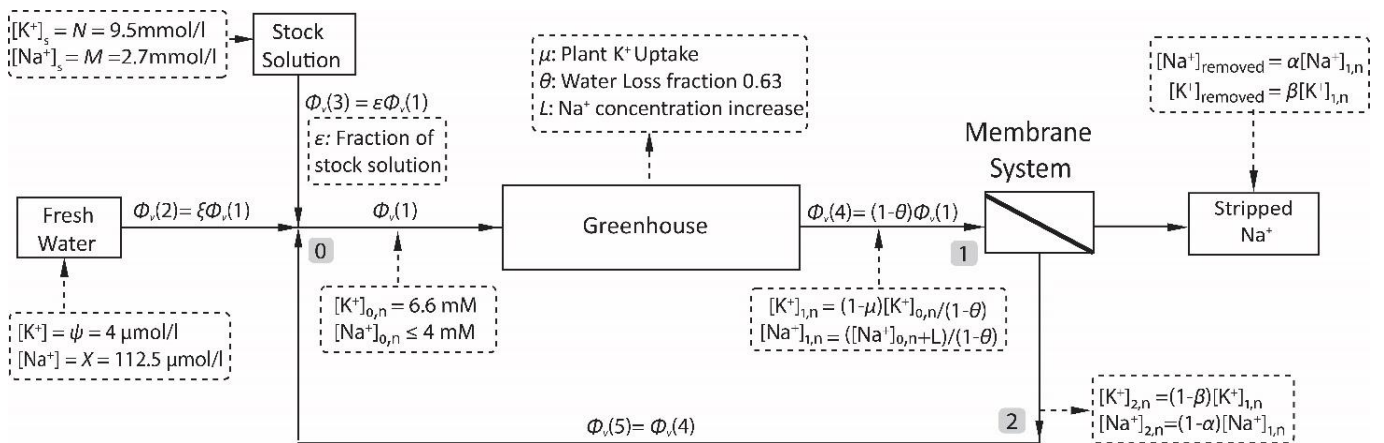
163 Because Na<sup>+</sup> is not taken up by the plants, it leaves the system only at the membrane  
164 unit. At the start of the first irrigation cycle the Na<sup>+</sup> concentration in the irrigation water  
165 is 1.9 mM (resulting from the background Na<sup>+</sup> concentrations in both fresh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

171 The membrane unit needs to remove Na<sup>+</sup> to meet a (steady-state) Na<sup>+</sup> concentration  
172 level in the irrigation water <20 mM, i.e., the upper tolerance level for Na<sup>+</sup> of tomato  
173 cultivation. Noteworthy, the model assumes that the membrane unit does not remove  
174 any water. The reason is that the LSM under development is composed of a hydrophobic  
175 support impregnated with a hydrophobic solvent containing the Na<sup>+</sup> selective carrier 15-  
176 crown-5. Prior to entering this organic phase, ions need to be dehydrated with the free  
177 energy ( $\Delta G$ ) of dehydration (>0) is compensated for by the  $\Delta G$  of ion coordination by the  
178 15-crown-5(<0). The water permeation through such LSM systems is negligible.

### 179 **2.3 Mass balances**

180 At the start of each new cycle, the addition of fresh water and fertilizer at reference  
181 point #0 has to compensate for the total water loss due to evapotranspiration and K<sup>+</sup>  
182 losses due to plant uptake and removal by the membrane unit. Together with the  
183 recycled fraction entering point #0, the fractions of added fresh water and stock solution

184 are adjusted such that the  $K^+$  concentration of the irrigation water entering the  
 185 greenhouse at point #0 is 6.6 mM. Given this fixed value of 6.6 mM, adjustment is  
 186 possible because the total fraction of fresh water and stock solution at point #0 is known  
 187 to be 1.0 for the first cycle ( $n=1$ ), and 0.63 for all subsequent cycles ( $n>1$ ). The  
 188 calculation of all parameters is thus based on the fraction of fertilizer stock solution ( $\varepsilon$ )  
 189 added at point #0. For that reason, we designated  $\varepsilon$  the master variable in our  
 190 simulations. On the same token,  $K^+$  is the master ionic species, dictating, by means of  $\varepsilon$ ,  
 191 the concentration of the slave ionic species  $Na^+$  at point #0 at the start of each new cycle.  
 192 Once  $\varepsilon$  has been calculated from the mass (or volumetric flow) balance at point #0, the  
 193  $Na^+$  concentration can be calculated as well.  
 194 For the very first water cycle, only stock solution and fresh water will meet at point #0.  
 195 From the second cycle on, however, recycled drain water will join these two water  
 196 streams at point #0. For this reason, the calculation of the first and the following cycles  
 197 should be considered separately.



198  
 199 **Figure 2.** Outline of Fig. 1 complemented with the volumetric flows  $\Phi_v(1)$ -  $\Phi_v(5)$  and the  
 200 process parameters indicated.

201 **2.3.1 Volumetric flow balance for the first two cycles**

202 **2.3.1.1 First irrigation cycle (n=1)**

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

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

206  
 207 **Table 1.** Description of the parameters used throughout this study, corresponding to  
 208 Figs. 1 and 2.

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

213

214

215 **Reference point #0**

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

223 The volumetric flow balance reads:

$$224 \Phi_v(1) = \Phi_v(2) + \Phi_v(3) = \xi_1 \Phi_v(1) + \varepsilon_1 \Phi_v(1) \quad (1)$$

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

$$227 [K^+]_{0,1} \times \Phi_v(1) = \Psi \times \xi_1 \Phi_v(1) + N \times \varepsilon_1 \Phi_v(1) \quad (2)$$

228 Because  $\xi_1 + \varepsilon_1 = 1$  and dividing by  $\Phi_v(1)$  renders for the K<sup>+</sup> concentration:

$$229 [K^+]_{0,1} = (1 - \varepsilon_1)\Psi + \varepsilon_1 N = \varepsilon_1(N - \Psi) + \Psi \quad (3)$$

230 The fraction of stock solution thus is:

$$231 \varepsilon_1 = ([K^+]_{0,1} - \Psi)/(N - \Psi) \quad (4)$$

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

233 Once  $\varepsilon_1$  is known, the Na<sup>+</sup> concentration for the first cycle can be calculated by:

$$234 [Na^+]_{0,1} = \xi_1 X + \varepsilon_1 M = \varepsilon_1(M - X) + X \quad (5)$$

235 where M and X are the Na<sup>+</sup> concentration of the stock solution and fresh water,  
236 respectively.

237 Compared to the K<sup>+</sup> concentration at point #0, the K<sup>+</sup> concentration at point #1 will be  
238 different due to K<sup>+</sup> uptake by the plants and evapotranspiration. Because [K<sup>+</sup>]<sub>0,n</sub> is fixed  
239 at 6.6 mM, [K<sup>+</sup>]<sub>1,n</sub> is directly proportional to [K<sup>+</sup>]<sub>0,n</sub>. Let  $\mu$  be the fraction of K<sup>+</sup> taken up by  
240 the plants and  $\theta$  the fraction of water loss due to evapotranspiration. Then, [K<sup>+</sup>]<sub>1,1</sub> is  
241 given by:

$$242 \quad [K^+]_{1,1} = [(1 - \mu)[K^+]_{0,1}]/(1 - \Theta) \quad (6)$$

243 The Na<sup>+</sup> concentration will also change, firstly, because of evapotranspiration, secondly  
244 because of the Na<sup>+</sup> that leaches out of the coconut-based substrate used, causing an  
245 increase of the Na<sup>+</sup> concentration, represented by L. Then [Na<sup>+</sup>]<sub>1,1</sub> is given by:

$$246 \quad [Na^+]_{1,1} = ([Na^+]_{0,1} + L)/(1 - \Theta) \quad (7)$$

247

## 248 **Reference point #2**

249 Reference point #2 is located downstream the membrane unit (permeate side) and  
250 calculation of the K<sup>+</sup> and Na<sup>+</sup> concentration at this point therefore requires  
251 implementation of the membrane characteristics. Let  $\alpha$  be the fraction of Na<sup>+</sup> (compared  
252 to reference point #1) that permeates the membrane (and with that removed from the  
253 system) and  $\beta$  the fraction of K<sup>+</sup> that permeates the membrane (also removed from the  
254 system). Then the K<sup>+</sup> and Na<sup>+</sup> concentrations are given by [K<sup>+</sup>]<sub>2,1</sub>=(1- $\beta$ )[K<sup>+</sup>]<sub>1,1</sub> and

255 [Na<sup>+</sup>]<sub>2,1</sub>=(1- $\alpha$ )[Na<sup>+</sup>]<sub>1,1</sub>, respectively.

256

257 **2.3.1.2 Second irrigation cycle (n=2)**

258 The calculations for the second cycle are essentially the same as those for the first cycle.

259 The main difference concerns the starting point, i.e., the volumetric flow balance at point

260 #0, now given by:

$$261 \quad \Phi_v(1) = \Phi_v(2) + \Phi_v(3) + \Phi_v(5) \quad (8)$$

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

$$263 \quad \Phi_v(1) = \xi_2 \Phi_v(1) + \varepsilon_2 \Phi_v(1) + (1 - \theta) \Phi_v(1) \quad (9)$$

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

$$265 \quad \phi(v, 1) = (\theta - \varepsilon_2) \phi(v, 1) + \varepsilon_2 \phi(v, 1) + (1 - \theta) \phi(v, 1) \quad (10)$$

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

$$267 \quad [K^+]_{0,2} = \xi_2 \Psi + \varepsilon_2 N + (1 - \theta) [K^+]_{2,1} = (\theta - \varepsilon_2) \Psi + \varepsilon_2 N + (1 - \theta) [K^+]_{2,1} \quad (11)$$

$$268 \quad \varepsilon_2 = ([K^+]_{0,2} - (1 - \theta) [K^+]_{2,1} - \theta \Psi) / (N - \Psi) \quad (12)$$

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

$$270 \quad [Na^+]_{0,2} = \varepsilon_2 (M - X) + \theta X + (1 - \theta) [Na^+]_{2,1} \quad (13)$$

$$271 \quad [Na^+]_{1,2} = \frac{[\varepsilon_2 (M - X) + \theta X] + L}{1 - \theta} + [Na^+]_{2,1} \quad (14)$$

$$272 \quad [Na^+]_{2,2} = \frac{(1 - \alpha)}{(1 - \theta)} [\varepsilon_2 (M - X) + \theta X + L] + (1 - \alpha) [Na^+]_{2,1} \quad (15)$$

273 Apart from the fact that  $[K^+]_{0,n}$  remains constant for  $n > 1$  (6.6 mM),  $[K^+]_{1,n}$  and  $[K^+]_{2,n}$  are

274 constant as well having (if assuming  $\beta = 0.1$ ) a value of 11.4 and 10.3 mM, respectively. In

275 addition, from the second cycle onwards  $\varepsilon_n$  remains constant as well and independent of

276  $n$ . This can be seen after, first, substituting  $\varepsilon_1$  into  $[K^+]_{2,1}$  followed by substituting  $[K^+]_{2,1}$   
 277 into  $\varepsilon_2$ , resulting in:

$$278 \quad \varepsilon_n = \frac{[K^+]_{0,n}(1-(1-\beta)(1-\mu))-\theta \times \Psi}{N-\Psi} \quad (16)$$

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

281

### 282 2.3.3 Generalized expressions

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

$$294 \quad [Na^+]_{0,n} = (M - X) \sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i}] + (X\theta + L) \sum_{i=1}^{n-2} [(1 - \alpha)^i] + (X +$$

$$295 \quad L)(1 - \alpha)^{(n-1)} + X\theta \quad (17)$$

$$296 \quad [Na^+]_{1,n} = \frac{1}{(1-\theta)} [\sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i}] + [(X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^{(i-1)}] + (1 - \alpha)^{(n-1)} \times$$

$$297 \quad (X + L)] \quad (18)$$



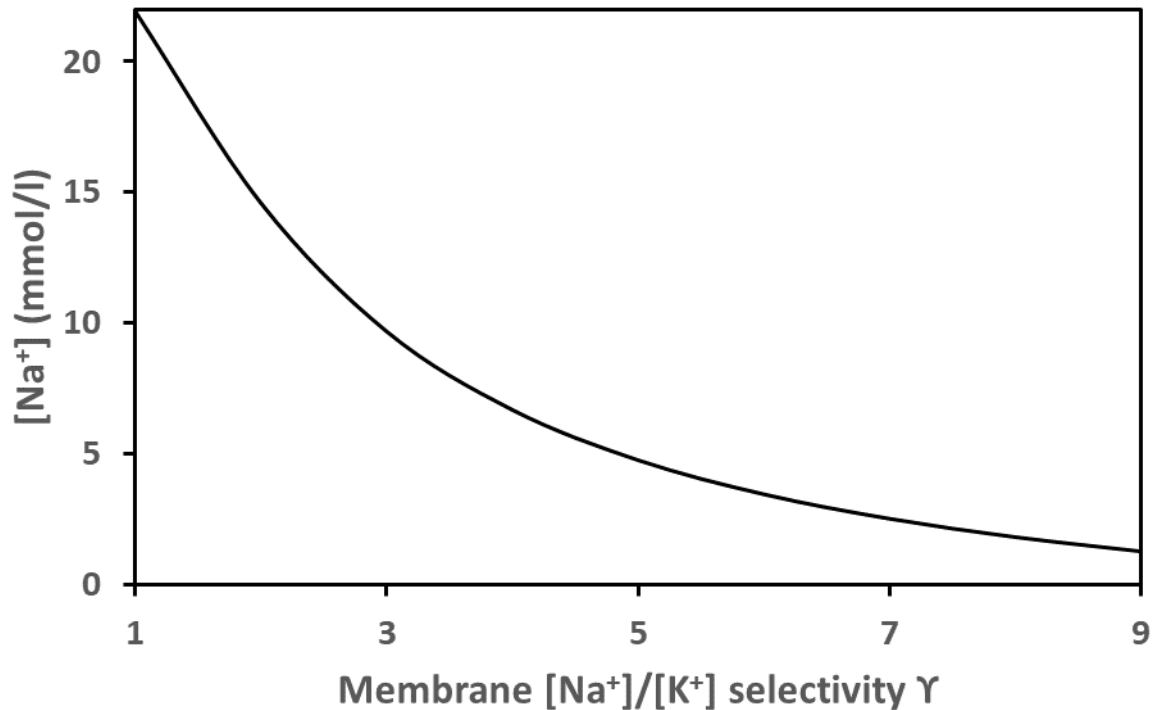
298 Note that for  $n=2$  and after a number of repeated substitutions, Eqs. 17 and 18 reduce to  
299 Eqs. 13 and 14, respectively.

## 300 **4. Results and discussion**

### 301 **4.1 Membrane selectivity**

302 The  $\text{Na}^+$  over  $\text{K}^+$  permeation selectivity also is an intrinsic membrane property. As stated  
303 previously, one of our prime goals is to determine the minimum membrane selectivity ( $\gamma$ )  
304 required to maintain the  $\text{Na}^+$  concentration in the IW below the upper tolerance level of  
305 4-5 mM. Because the membrane selectivity ( $\gamma$ ) is defined as the ratio of its permeability  
306 towards  $\text{Na}^+$  ( $\alpha$ ) and its permeability towards  $\text{K}^+$  ( $\beta$ ), the permeation of both ion species  
307 is coupled. With both  $\beta$  and  $\gamma$  set at a fixed value,  $\alpha$  can be calculated and with that the  
308  $\text{Na}^+$  level at point #2, which, in turn, allows the calculation of the  $\text{Na}^+$  level at point #0 at  
309 the start of a new cycle.

310 To compromise between minimizing  $\text{K}^+$  loss and dealing with a finite membrane  
311 selectivity, the value of  $\beta$  is set (arbitrarily) at 0.1, implying that 10% of  $\text{K}^+$  is removed  
312 together with  $\text{Na}^+$ . In combination with a membrane that does not discriminate between  
313  $\text{K}^+$  and  $\text{Na}^+$  ( $\gamma = 1$ ) this results in a  $\text{Na}^+$  removal of also 10%. In this case it is expected to  
314 see a dramatic  $\text{Na}^+$  accumulation in the IW. Figure 3 confirms this expectation showing  
315 the  $\text{Na}^+$  level in the IW after 10 cycles of operation and for a  $\text{Na}^+$  over  $\text{K}^+$  selectivity  
316 ranging from  $\gamma = 1$  to 9. Note that  $\gamma = 1$  indeed results in staggering  $\text{Na}^+$  concentrations  
317 after 10 cycles of operation.



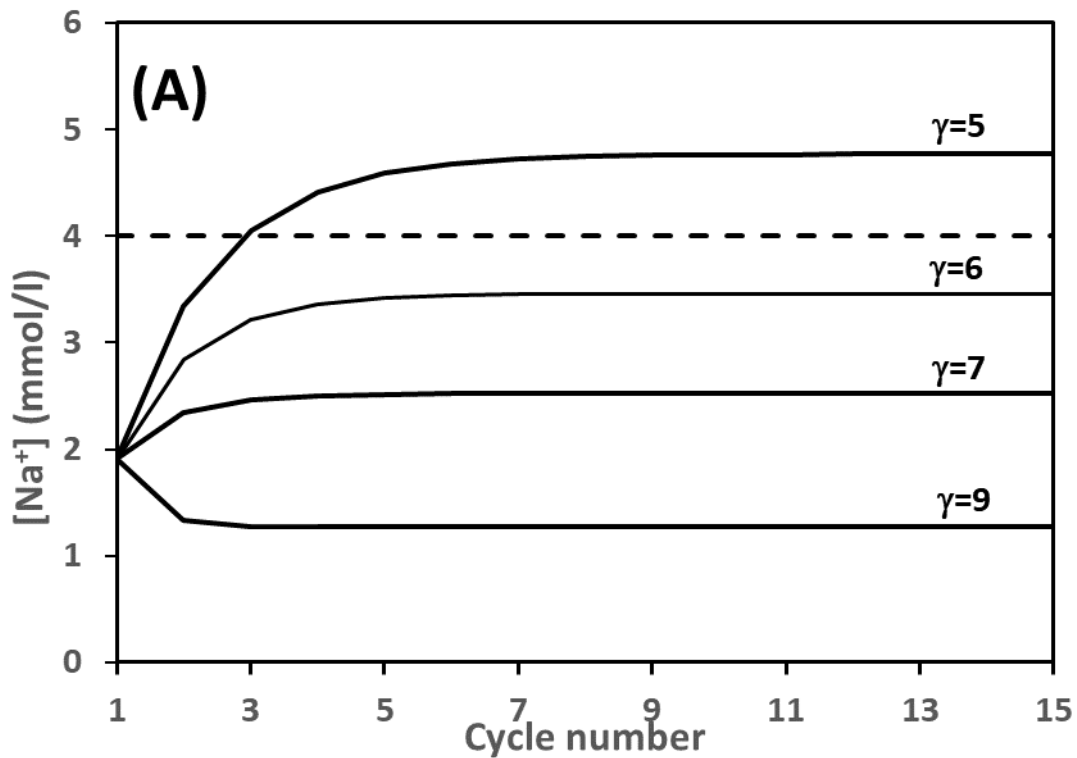
318

319 **Figure 3.** Accumulation of  $\text{Na}^+$  in the irrigation water entering the greenhouse (i.e., at  
 320 point #0) after 10 cycles of operation for a membrane with a  $\text{Na}^+/\text{K}^+$  selectivity ranging  
 321 from 1 to 9 and a  $\text{K}^+$  permeability  $\beta$  of 0.1, i.e., with 10% - 90% of the  $\text{Na}^+$  and 10% of the  
 322  $\text{K}^+$  removed.

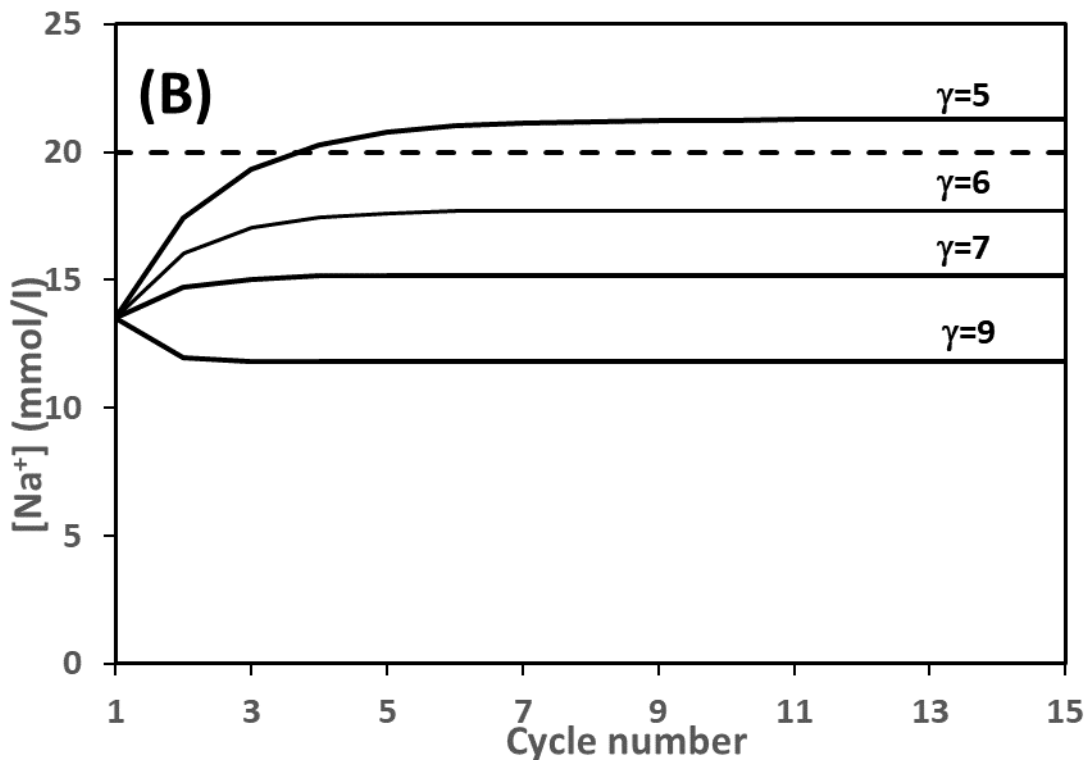
323

324 Figure 4 explores the relationship between membrane selectivity and the  $\text{Na}^+$  level at  
 325 points #0 and #1 during 15 subsequent cycles of operation, given the 10% removal of  $\text{K}^+$   
 326 ( $\beta = 0.1$ ) and for a  $\text{Na}^+$  over  $\text{K}^+$  membrane permeability selectivity ranging from 5 to 9. A  
 327 membrane selectivity of 5 does not suffice to achieve a steady-state  $[\text{Na}^+]$  below the  
 328 threshold of 4 mM at point #0 (A) and of 20 mM at point #1 (B). Indeed, it requires at  
 329 least a selectivity of 6 to accomplish steady-state levels remaining below these  
 330 thresholds. As indicated in Fig. 2,  $\text{Na}^+$  is entering the system from three sources, the  
 331 fresh water, the fertilizer content and the  $\text{Na}^+$  leaching from the coconut-based substrate  
 332 used. As already remarked, from the second cycle on  $\varepsilon_n$  adopts a constant numerical  
 333 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  
 334 amount of  $\text{Na}^+$  entering the system from the fresh water and fertilizer is 3 and 72 g/hr,

335 respectively. The  $\text{Na}^+$  concentration increase due to leaching equals 3.1 mM, resulting in  
336 285 g/hr. Evidently, at steady state the total amount of 360 gr/hr equals the amount of  
337  $\text{Na}^+$  that needs to be removed by the membrane unit.



338



339

340 **Figure 4.** (A). [Na<sup>+</sup>] in the irrigation water entering the greenhouse at point #0; (B). [Na<sup>+</sup>]  
 341 in the irrigation water leaving the greenhouse at point #1 during 15 cycles of operation,  
 342 for a Na<sup>+</sup>/K<sup>+</sup> membrane selectivity ranging from 5 to 9 and a K<sup>+</sup> permeability  $\beta$  of 0.1,  
 343 i.e., with 50% - 90% of the Na<sup>+</sup> and 10% of the K<sup>+</sup> removed. Dotted lines represent the  
 344 threshold of 4 mM of the Na<sup>+</sup> content of the IW entering the greenhouse (A) and the  
 345 physiological tolerance threshold for tomato of 20 mM (B).

346

347 In order to maintain a steady-state  $K^+$  concentration in the IW of 6.6 mM, the added  
348 amount of  $K^+$ , originating from the fertilizer, equals  $\varepsilon_n \times N \times \Phi_v(1) = 430$  g/hr.

349

### 350 **4.3 Implementation**

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

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

$$362 \quad A = Q \times F \times ([Na^+]_{1,2} - [Na^+]_{2,2}) / if \quad (19)$$

363 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  
364 before, any water flow arising from either osmosis or electro osmosis is ignored, given  
365 the strong hydrophobic nature of the LSM system. According to Fig. 2 and given  $\alpha=0.6$   
366 and  $\beta=0.1$  (Fig. 4A with  $\gamma=6$ ),  $[Na^+]_{0,n}$  reaches a steady-state value of 3.45 mM. The  
367 difference between the  $Na^+$  concentration of the solution entering and leaving the  
368 membrane then is  $0.6 \times (3.5 + 3.1) / 0.37 = 10.7$  mM. Note that this concentration difference  
369 results in  $10.7 \times 10^{-3} \times 23 \times 4000 \times 0.37 = 365$  gr  $Na^+$ /hr that needs to be removed, essentially  
370 the same amount as previously derived from the amount of  $Na^+$  entering the system. As

371 for the current density, we take a 'typical' value for ion exchange membranes given a  
372 total ionic strength of the incoming water of around 25-30 mM, i.e., 10 A/m<sup>2</sup> [23].  
373 Further, as a rather conservative estimate the current utilization factor ( $f$ ) is assumed to  
374 be 0.6, implying that 60% of the current is actually carried by Na<sup>+</sup>, the remaining 40% by  
375 K<sup>+</sup> and other ion species present. Substituting these numbers in Eq. 19 renders a  
376 membrane surface area of 70 m<sup>2</sup>. In practice, this could be achieved by constructing ED  
377 stacks with a number of cells in series. For instance, three ED modules, each comprising  
378 of a stack of 12 cells with a membrane surface area of 2 m<sup>2</sup> each.

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

### 388 **4.3 Economics perspective**

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

393 Firstly, the capital cost of the LSM currently developed and validated is to a large extent  
394 dominated by the amount of 15-crown-5 needed. When purchased from TCI-Chemicals

395 and given the 15-crown-5 density (0.2 M), the membrane thickness (100  $\mu\text{m}$ ) and a  
396 support porosity of 50% the estimated cost price amounts to 78 euro per  $\text{m}^2$ . To put this  
397 number in perspective, the price of typical commercially available ion exchange  
398 membranes is around 30 euro per  $\text{m}^2$ . The most promising options to bring the price  
399 from the LSM down, seem a thinner membrane and upscaling 15-crown-5 (in-house)  
400 synthesis. It should be mentioned however that the (at this moment unknown and  
401 therefore not considered here) manufacturing cost contribute significantly to if not  
402 dominate the cost prize (Fuji Film, Netherlands; personal communication).

403 Secondly, the operational costs on the other hand will be dominated by the power  
404 needed to run the system. Based on the specifications of a typical ED system and given  
405 the salt concentration in the feed, the power consumption will be in the range 0.7 – 2.5  
406  $\text{kWh/m}^3$  [24]. The power consumption is linear with the applied current density [22]  
407 and as evident from Eq. 19, there are essentially three ways to reduce the required total  
408 membrane surface area: by reducing the volumetric flow through the system, by  
409 increasing the current utilization factor or by increasing the current density. Reduction  
410 of the volumetric flow could (possibly) be accomplished by a different configuration  
411 altogether. For instance, by positioning the membrane module not in the main stream  
412 (as in Figs. 1, 2) but instead in a bypass. This option will be explored in more detail once  
413 we (experimentally) obtained the actual specifications of our membrane under  
414 development. Improving the current utilization factor implies a higher  $\text{Na}^+$  over  $\text{K}^+$   
415 membrane selectivity. Even though the cost for re-supplementing the IW with  $\text{K}^+$  will go  
416 down, the membrane itself will (probably) be more expensive due to the higher density  
417 of crown ethers required. Finally, a higher current density will reduce the total  
418 membrane surface area needed but increase the power needed during operation. As  
419 pointed out by Strathmann [22], the opposite effect of current density on required

420 membrane surface area and energy cost may translate in an optimal current density,  
421 resulting in the lowest overall costs.

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

## 428 **5. Conclusion**

429 Excess Na<sup>+</sup> in irrigation water needs to be removed to a level dictated by the tolerance  
430 threshold specific for the particular crop, for tomato 20 mM. The closed-loop irrigation  
431 water system described here includes a membrane-based module to remove excess Na<sup>+</sup>  
432 while preserving the (nutrient) K<sup>+</sup> as much as possible. Based on real-life process  
433 parameters, the present study indicates that a Na<sup>+</sup> over K<sup>+</sup> membrane permeation  
434 selectivity of 6 already suffices to remain the Na<sup>+</sup> level the plants are exposed to below  
435 20 mM, at least if accepted that 10% of the K<sup>+</sup> is removed as well. If implemented in an  
436 electro dialysis set-up while assuming a constant current density of 10 A/m<sup>2</sup>, the  
437 estimated total membrane surface is 70 m<sup>2</sup>. Considering the opposite effect of current  
438 density on required membrane surface area and energy cost, an optimum current  
439 density is hypothesized, resulting in a minimum of overall cost.

## 440 **Conflict of Interest Statement**

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



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### 523 **Supporting information**

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

526 *Z. Qian* <sup>a,c</sup>, *H. Miedema* <sup>c</sup>, *L.C.P.M. de Smet* <sup>b,c</sup>, *E.J.R. Sudhölter* <sup>a</sup>

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

530 The manuscript gives the equations for  $\varepsilon$  and the  $K^+$  and  $Na^+$  concentrations during the  
531 1<sup>st</sup> and 2<sup>nd</sup> cycle of operation. Here the expressions for the  $Na^+$  concentrations at the  
532 three reference points during the 2<sup>nd</sup> cycle are given again but, in contrast to the  
533 manuscript, this time exclusively in terms of known parameters, as required to derive  
534 the generalized expressions.

$$535 [Na^+]_{0,2} = (M - X)[\varepsilon_2 + \varepsilon_1(1 - \alpha)] + (X + L)(1 - \alpha) + \theta X$$

536 (1)

$$537 [Na^+]_{1,2} = [(M - X)[\varepsilon_2 + \varepsilon_1(1 - \alpha)] + (X + L)(1 - \alpha) + \theta X + L]/(1 - \theta)$$

538 (2)

$$[Na^+]_{2,2} =$$

$$[(M - X)[\varepsilon_2(1 - \alpha) + \varepsilon_1(1 - \alpha)^2] + (X + L)(1 - \alpha)^2 + (\theta X + L)(1 - \alpha)]/(1 - \theta)$$

539  
540

541 (3)

542 As shown in the manuscript (Eq. 16), from the 2<sup>nd</sup> cycle on  $\varepsilon_n$  becomes constant:

$$543 \varepsilon_n = \frac{[K^+]_{0,n}(1 - (1 - \beta)(1 - \mu)) - \theta \times \Psi}{N - \Psi} \quad (4)$$

544

545 Apart from the fact that  $[K^+]_{0,n}$  remains constant for  $n > 1$  (6.6 mM),  $[K^+]_{1,n}$  and  $[K^+]_{2,n}$  are  
546 constant as well having (if assuming  $\beta = 0.1$ ) a value of 11.4 and 10.3 mM, respectively.  
547 For this reason, this Supplement is restricted to the  $Na^+$  level at each reference point for  
548  $n > 2$ .

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

550 **Reference point #0**

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

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

552  
553 (5)

554 **Reference point #1**

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

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

556  
557 (6)

558

559 **Reference point #2**

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

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

561  
562 (7)

563

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

565 **Reference point #0**

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

566  
567 (8)

568 **Reference point #1**

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

569  
570 (9)

571 **Reference point #2**

572  $[\text{Na}^+]_{2,4} = [(M - X) \times [\varepsilon_4(1 - \alpha) + \varepsilon_3(1 - \alpha)^2 + \varepsilon_2(1 - \alpha)^3 + \varepsilon_1(1 - \alpha)^4]] + (1 - \alpha)^4 \times$   
 573  $(X + L) + (1 - \alpha)^3(X\theta + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L)] / (1 - \theta)$   
 (10)

574

575

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

577 ***Reference point #0***

578  $[\text{Na}^+]_{0,5} = (M - X) \times [\varepsilon_5 + \varepsilon_4(1 - \alpha) + \varepsilon_3(1 - \alpha)^2 + \varepsilon_2(1 - \alpha)^3 + \varepsilon_1(1 - \alpha)^4] +$   
 579  $(1 - \alpha)^4(X + L) + (1 - \alpha)^3(X\theta + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta$   
 580 (11)

581

582 ***Reference point #1***

583  $[\text{Na}^+]_{1,5} = [(M - X) \times [\varepsilon_5 + \varepsilon_4(1 - \alpha) + \varepsilon_3(1 - \alpha)^2 + \varepsilon_2(1 - \alpha)^3 + \varepsilon_1(1 - \alpha)^4]] +$   
 584  $(1 - \alpha)^4(X + L) + (1 - \alpha)^3(X\theta + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta +$   
 $L] / (1 - \theta)$   
 (12)

585 ***Reference point #2***

586  $[\text{Na}^+]_{2,5} = [(M - X) \times [\varepsilon_5(1 - \alpha) + \varepsilon_4(1 - \alpha)^2 + \varepsilon_3(1 - \alpha)^3 + \varepsilon_2(1 - \alpha)^4 +$   
 587  $\varepsilon_1(1 - \alpha)^5]] + (1 - \alpha)^5(X + L) + (1 - \alpha)^4(X\theta + L) + (1 - \alpha)^3(X\theta + L) +$   
 $(1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L)] / (1 - \theta)$   
 (13)

588 **Generalized expressions for the n<sup>th</sup> irrigation cycle (n≥2)**

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

592  $[\text{Na}^+]_{0,n} = (M - X) \sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i}] + (X\theta + L) \sum_{i=1}^{n-2} [(1 - \alpha)^i] + (X + L) \times$   
 593  $(1 - \alpha)^{(n-1)} + X\theta$   
 (14)

594 Using the generalized form of Eq. 7 in the manuscript:

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

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

597 
$$[\text{Na}^+]_{1,n} = \frac{1}{(1-\theta)} [(M - X) \sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i}] + [(X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^{(i-1)}] +$$

598  $(1 - \alpha)^{(n-1)} \times (X + L)]$   
(15)

599

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

601

602 
$$[\text{Na}^+]_{1,n} = \frac{1}{(1-\theta)} [(M - X) \sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i+1}] + [(X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^i] +$$

603  $(1 - \alpha)^n \times (X + L)]$   
(16)

604

605

# 1 **Modelling the Selective Removal of Sodium Ions from** 2 **Greenhouse Irrigation Water Using Membrane Technology**

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## 11 **Abstract**

12 A model is presented for the Na<sup>+</sup> and K<sup>+</sup> levels in the irrigation water of greenhouses,  
13 specifically those for the cultivation of tomato. The model, essentially based on mass  
14 balances, not only describes the accumulation of Na<sup>+</sup> but includes a membrane unit for  
15 the selective removal of Na<sup>+</sup> as well. As determined by the membrane properties, some  
16 of the K<sup>+</sup> is removed as well. Based on real-life process parameters, the model calculates  
17 the Na<sup>+</sup> and K<sup>+</sup> concentration at three reference points. These process parameters  
18 include the evapotranspiration rate, the K<sup>+</sup> uptake by the plants, the Na<sup>+</sup> and K<sup>+</sup> content  
19 of the fertilizer, the Na<sup>+</sup> leaching out from the hydroponic substrate material, and the  
20 Na<sup>+</sup> and K<sup>+</sup> removal efficiency of the membrane unit. Using these parameters and given a  
21 constant K<sup>+</sup> concentration of the irrigation water entering the greenhouse of 6.6 mM  
22 (resulting in the optimal K<sup>+</sup> concentration for tomato cultivation), the composition of the  
23 solution is completely defined at all three reference points per irrigation cycle. Prime  
24 aim of this investigation is to explore the requirements for the selective membrane that

25 currently is developed in our lab. It is found that even for a limited  $\text{Na}^+$  over  $\text{K}^+$   
26 selectivity of 6, after a number of cycles the  $\text{Na}^+$  level reaches steady state at a level  
27 below the upper (toxic) threshold for tomato cultivation (20 mM). Economic aspects and  
28 ways of implementation of such a system are briefly discussed.

## 29 **Keywords**

30 Greenhouse; Irrigation water; Sodium removal; Mass balance; Modelling;  $\text{Na}^+$  over  $\text{K}^+$   
31 membrane selectivity

## 32 **1. Introduction**

33 Closed-loop soilless or hydroponic systems are already widely used if not, at least in  
34 certain countries e.g. The Netherlands, common practice in horticulture[1]. Nutrients  
35 and water are supplied continuously to the irrigation water (IW) to compensate for  
36 nutrient uptake by the plants and water loss due to evapotranspiration. Ideally, the  
37 nutrient and water supply are fine-tuned such that the nutrient concentration and the  
38 osmotic pressure of the drainage solution remain (fairly) constant. Consequently,  
39 nutrients, which are present but are not taken up by the plant, accumulate in the IW.  $\text{Na}^+$   
40 is a typical example of an ion that over time builds up in the IW [2]. High  $\text{Na}^+$  levels  
41 inhibit plant growth directly or indirectly by hampering the uptake of other nutrients [3-  
42 6]. Because of the detrimental effects of high  $\text{Na}^+$ , the IW  $\text{Na}^+$  level has been subject of  
43 numerous studies already [7-9]. These studies are restricted however to simulation  
44 studies, validated or not by monitoring the actual  $\text{Na}^+$  level in the IW during crop growth.  
45 Despite the detrimental effects at higher levels, plants do show a certain tolerance for  
46  $\text{Na}^+$ . Reported  $\text{Na}^+$  threshold values for tomato vary somewhat but levels above 5 dS/m,  
47 equivalent to 50 mM, prove to inhibit growth and yield [10]. The threshold value might



48 depend on the tomato species; the value used in the present study is 20 mM. As soon as  
49  $\text{Na}^+$  exceeds the threshold level, the IW is discharged and needs to be renewed. After  
50 replenishing the system with freshly prepared IW the entire process of  $\text{Na}^+$  building up  
51 starts all over again. Our goal is, apart from monitoring, to develop a (membrane-based)  
52 system that selectively removes accumulated  $\text{Na}^+$  from the IW. A complication arises  
53 from the fact that  $\text{K}^+$ , an essential plant nutrient, has very similar physicochemical  
54 properties as  $\text{Na}^+$ . Both (alkali metal) ion species have the same valence (+1) and are  
55 similar in size with ionic radii of 1.90 and 2.43 Ångstrom for  $\text{Na}^+$  and  $\text{K}^+$ , respectively.  
56 However, a key (physiological) difference between the two ion species is that  $\text{Na}^+$  is  
57 hardly taken up by the plant and is the major cause of salinity toxicity [11, 12]. Excess  
58  $\text{Na}^+$  thus needs to be removed, either by resin-based absorbance technology or  
59 membrane technology. The latter is preferred because it circumvents the necessity of  
60 resin regeneration once it has become saturated with  $\text{Na}^+$ .

61 The fact that  $\text{Na}^+$  and  $\text{K}^+$  behave very much the same because they share similar  
62 physicochemical properties is exactly the reason that there are no commercial  
63 separation membranes available yet that discriminate between the two ion species. Here  
64 separation refers to a membrane that allows high fluxes. Selective membranes for ion  
65 selective electrodes (ISE) do exist already. However, ion fluxes over such *potentiometric*  
66 membranes are by definition essentially zero [13, 14]. Ceramic NASICON-based  
67 membranes do selectively transport  $\text{Na}^+$  [15]. However, only harsh operational  
68 conditions like high temperature or high acidity or alkalinity justify their use because of  
69 the high price. In addition, the high conductivity demonstrated in battery applications  
70 remains relatively low compared to the conductivity of typical polymeric ion exchange  
71 membranes [16].

72 To impose selectivity on a polymeric or Liquid Supported Membrane (LSM), a compound  
73 is blended in with the membrane polymer or a mobile carrier is added to the organic  
74 phase of the LSM [17, 18, 19]. Na<sup>+</sup> selective carriers include natural monensin and the  
75 synthetic crown ether 15-crown-5. Monensin has been used for ISE applications as well  
76 as for Na<sup>+</sup> extraction by ionic liquids enriched with monensin [20, 21]. Current focus of  
77 our lab is on developing a LSM-based system with the organic phase supplemented with  
78 15-crown-5.

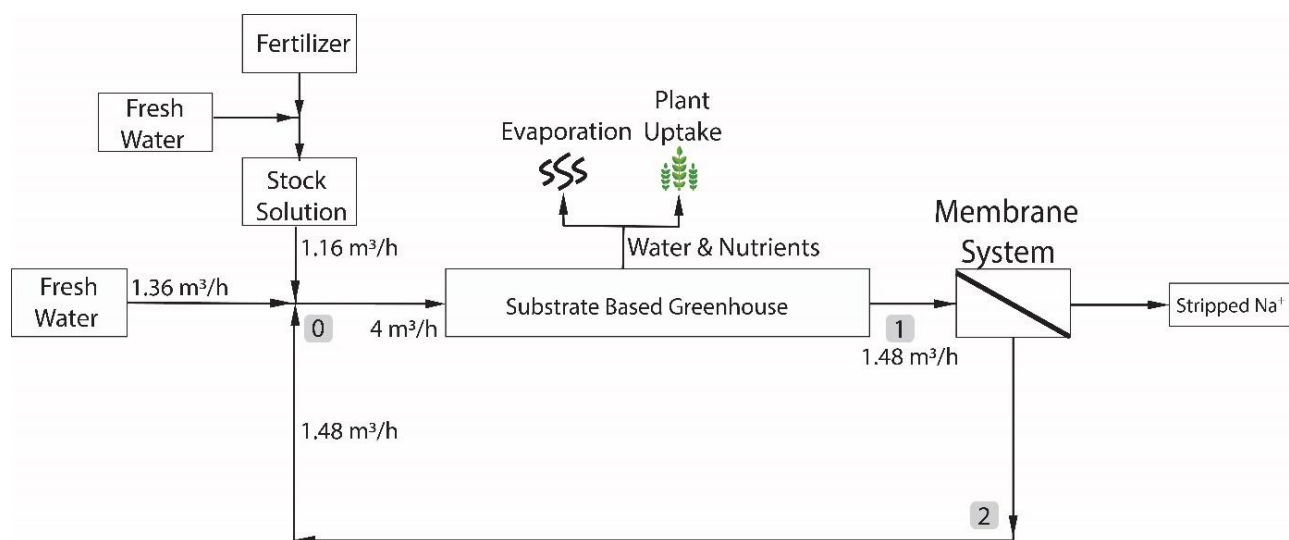
79 The technological challenge thus is to develop a separation membrane that permeates  
80 Na<sup>+</sup> but not, or at least to a much lower extent, K<sup>+</sup>. Obviously, the less permeable for K<sup>+</sup>,  
81 the less K<sup>+</sup> needs to be re-supplied to compensate for this loss. Therefore,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

97 discharge of K<sup>+</sup>. The membrane specifications resulting from the present analysis will  
98 guide us in the currently performed investigation to actually fabricate such a membrane  
99 system.

## 100 **2. Material & Methods**

### 101 **2.1 System & Model Design**

102 The greenhouse recycling system considered in the present study is schematically  
103 shown in Fig. 1. The fresh water source is accumulated rainwater whereas dissolved  
104 fertilizer is added as stock solution with a composition adjusted to the requirement of  
105 the particular greenhouse crop. Also indicated in Fig. 1 is the membrane unit  
106 responsible for Na<sup>+</sup> removal and producing a waste stream of Na<sup>+</sup>. Depending on the  
107 membrane selectivity, this waste stream is to a more or lesser extent contaminated with  
108 K<sup>+</sup>. Along the process line, three reference points are distinguished: point #0 where  
109 fresh water, stock solution and recycled drain water are mixed forming fresh (i.e., next  
110 cycle) irrigation water entering the greenhouse; #1 the drain water leaving the  
111 greenhouse before it enters the membrane module and #2 the drain water after  
112 filtration by the membrane unit. The model aims to calculate the Na<sup>+</sup> and K<sup>+</sup>  
113 concentrations during each cycle ( $n$ ) at the three reference points indicated. The  
114 nomenclature practiced throughout this study is based on the use of two indices, the  
115 first representing the reference point, the second the cycle number. For instance, [K<sup>+</sup>]<sub>2,3</sub>  
116 refers to the K<sup>+</sup> concentration at reference point #2 during the third cycle.



117  
 118 **Figure 1.** Outline of a substrate-based greenhouse irrigation water system with the  
 119 drain water recycled and including a membrane unit for the selective removal of Na<sup>+</sup>.  
 120 Reference points #0-2 are indicated as well as the relevant (steady-state) volumetric  
 121 flows while assuming a K<sup>+</sup> loss of 10% (i.e.,  $\beta=0.1$ ).

122  
 123 **2.2 Process parameters**

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

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

132 *Fresh water.* Since rainwater is used as fresh water source at reference point #0, three  
 133 sets of samples were collected during September-October-2017 at Wetsus in  
 134 Leeuwarden, the Netherlands. The K<sup>+</sup> and Na<sup>+</sup> levels were analyzed using inductively  
 135 coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 5000  
 136 Series). All required dilutions were carried out with ultrapure water (Millipore

137 purification unit). The average K<sup>+</sup> and Na<sup>+</sup> concentration in rain water was 158 µg/l and  
138 2587 µg/l, resulting in background concentrations of 4 µM and 112.5 µM for K<sup>+</sup> and Na<sup>+</sup>,  
139 respectively.

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

145 *K<sup>+</sup> concentration*. K<sup>+</sup> enters the system from two potential sources:

- 146 1) The background K<sup>+</sup> concentration in fresh water (4 µM), and
- 147 2) The K<sup>+</sup> content of the fertilizer stream (9.5 mM).

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

$$157 \mu = 1 - \frac{11.4 \times (1 - 0.63)}{6.6} = 0.36$$

158 *Na<sup>+</sup> concentration*. Na<sup>+</sup> enters the system from three potential sources:

- 159 1) The background Na<sup>+</sup> concentration in fresh water (112.5 µM),

160 2) The  $\text{Na}^+$  content of the fertilizer (2.7 mM), and  
161 3) The  $\text{Na}^+$  leaching from the (coconut-based) substrate material used in the greenhouse,  
162 leads to a  $\text{Na}^+$  enrichment of the irrigation water (*vide infra*).

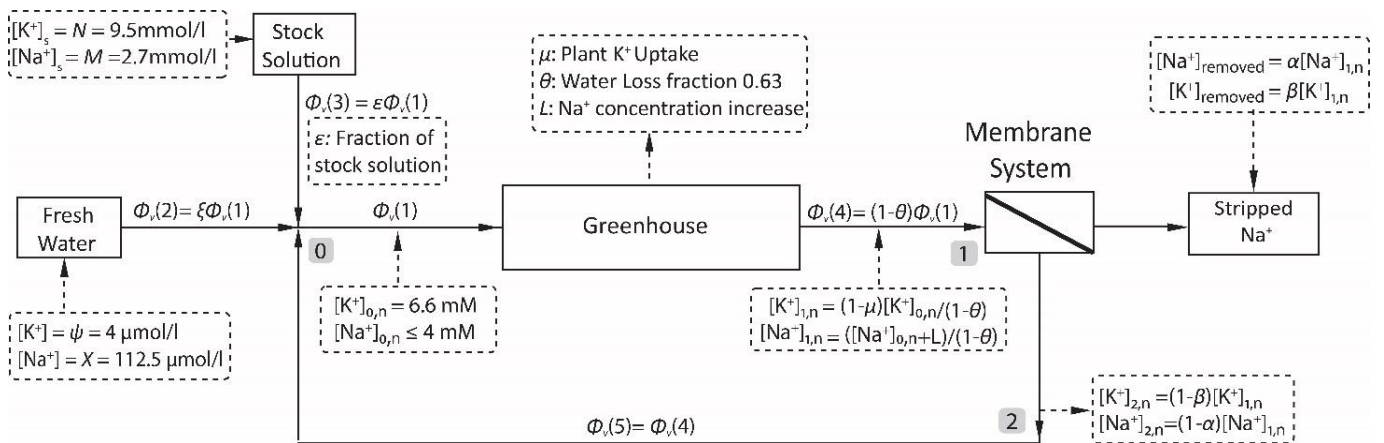
163 Because  $\text{Na}^+$  is not taken up by the plants, it leaves the system only at the membrane  
164 unit. At the start of the first irrigation cycle the  $\text{Na}^+$  concentration in the irrigation water  
165 is 1.9 mM (resulting from the background  $\text{Na}^+$  concentrations in both fresh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

171 The membrane unit needs to remove  $\text{Na}^+$  to meet a (steady-state)  $\text{Na}^+$  concentration  
172 level in the irrigation water  $<20$  mM, i.e., the upper tolerance level for  $\text{Na}^+$  of tomato  
173 cultivation. Noteworthy, the model assumes that the membrane unit does not remove  
174 any water. The reason is that the LSM under development is composed of a hydrophobic  
175 support impregnated with a hydrophobic solvent containing the  $\text{Na}^+$  selective carrier 15-  
176 crown-5. Prior to entering this organic phase, ions need to be dehydrated with the free  
177 energy ( $\Delta G$ ) of dehydration ( $>0$ ) is compensated for by the  $\Delta G$  of ion coordination by the  
178 15-crown-5 ( $<0$ ). The water permeation through such LSM systems is negligible.

### 179 2.3 Mass balances

180 At the start of each new cycle, the addition of fresh water and fertilizer at reference  
181 point #0 has to compensate for the total water loss due to evapotranspiration and  $\text{K}^+$   
182 losses due to plant uptake and removal by the membrane unit. Together with the  
183 recycled fraction entering point #0, the fractions of added fresh water and stock solution

184 are adjusted such that the  $K^+$  concentration of the irrigation water entering the  
 185 greenhouse at point #0 is 6.6 mM. Given this fixed value of 6.6 mM, adjustment is  
 186 possible because the total fraction of fresh water and stock solution at point #0 is known  
 187 to be 1.0 for the first cycle ( $n=1$ ), and 0.63 for all subsequent cycles ( $n>1$ ). The  
 188 calculation of all parameters is thus based on the fraction of fertilizer stock solution ( $\varepsilon$ )  
 189 added at point #0. For that reason, we designated  $\varepsilon$  the master variable in our  
 190 simulations. On the same token,  $K^+$  is the master ionic species, dictating, by means of  $\varepsilon$ ,  
 191 the concentration of the slave ionic species  $Na^+$  at point #0 at the start of each new cycle.  
 192 Once  $\varepsilon$  has been calculated from the mass (or volumetric flow) balance at point #0, the  
 193  $Na^+$  concentration can be calculated as well.  
 194 For the very first water cycle, only stock solution and fresh water will meet at point #0.  
 195 From the second cycle on, however, recycled drain water will join these two water  
 196 streams at point #0. For this reason, the calculation of the first and the following cycles  
 197 should be considered separately.



198  
 199 **Figure 2.** Outline of Fig. 1 complemented with the volumetric flows  $\Phi_v(1)$ -  $\Phi_v(5)$  and the  
 200 process parameters indicated.

201 **2.3.1 Volumetric flow balance for the first two cycles**

202 **2.3.1.1 First irrigation cycle (n=1)**

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

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

206  
 207 **Table 1.** Description of the parameters used throughout this study, corresponding to  
 208 Figs. 1 and 2.

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

213

214



215 **Reference point #0**

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

223 The volumetric flow balance reads:

$$224 \Phi_v(1) = \Phi_v(2) + \Phi_v(3) = \xi_1 \Phi_v(1) + \varepsilon_1 \Phi_v(1) \quad (1)$$

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

$$227 [K^+]_{0,1} \times \Phi_v(1) = \Psi \times \xi_1 \Phi_v(1) + N \times \varepsilon_1 \Phi_v(1) \quad (2)$$

228 Because  $\xi_1 + \varepsilon_1 = 1$  and dividing by  $\Phi_v(1)$  renders for the K<sup>+</sup> concentration:

$$229 [K^+]_{0,1} = (1 - \varepsilon_1)\Psi + \varepsilon_1 N = \varepsilon_1(N - \Psi) + \Psi \quad (3)$$

230 The fraction of stock solution thus is:

$$231 \varepsilon_1 = ([K^+]_{0,1} - \Psi)/(N - \Psi) \quad (4)$$

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

233 Once  $\varepsilon_1$  is known, the Na<sup>+</sup> concentration for the first cycle can be calculated by:

$$234 [Na^+]_{0,1} = \xi_1 X + \varepsilon_1 M = \varepsilon_1(M - X) + X \quad (5)$$

235 where M and X are the Na<sup>+</sup> concentration of the stock solution and fresh water,  
236 respectively.

237 Compared to the K<sup>+</sup> concentration at point #0, the K<sup>+</sup> concentration at point #1 will be  
238 different due to K<sup>+</sup> uptake by the plants and evapotranspiration. Because [K<sup>+</sup>]<sub>0,n</sub> is fixed  
239 at 6.6 mM, [K<sup>+</sup>]<sub>1,n</sub> is directly proportional to [K<sup>+</sup>]<sub>0,n</sub>. Let  $\mu$  be the fraction of K<sup>+</sup> taken up by  
240 the plants and  $\theta$  the fraction of water loss due to evapotranspiration. Then, [K<sup>+</sup>]<sub>1,1</sub> is  
241 given by:

$$242 \quad [K^+]_{1,1} = [(1 - \mu)[K^+]_{0,1}]/(1 - \Theta) \quad (6)$$

243 The Na<sup>+</sup> concentration will also change, firstly, because of evapotranspiration, secondly  
244 because of the Na<sup>+</sup> that leaches out of the coconut-based substrate used, causing an  
245 increase of the Na<sup>+</sup> concentration, represented by L. Then [Na<sup>+</sup>]<sub>1,1</sub> is given by:

$$246 \quad [Na^+]_{1,1} = ([Na^+]_{0,1} + L)/(1 - \Theta) \quad (7)$$

247

## 248 **Reference point #2**

249 Reference point #2 is located downstream the membrane unit (permeate side) and  
250 calculation of the K<sup>+</sup> and Na<sup>+</sup> concentration at this point therefore requires  
251 implementation of the membrane characteristics. Let  $\alpha$  be the fraction of Na<sup>+</sup> (compared  
252 to reference point #1) that permeates the membrane (and with that removed from the  
253 system) and  $\beta$  the fraction of K<sup>+</sup> that permeates the membrane (also removed from the  
254 system). Then the K<sup>+</sup> and Na<sup>+</sup> concentrations are given by [K<sup>+</sup>]<sub>2,1</sub>=(1- $\beta$ )[K<sup>+</sup>]<sub>1,1</sub> and

255 [Na<sup>+</sup>]<sub>2,1</sub>=(1- $\alpha$ )[Na<sup>+</sup>]<sub>1,1</sub>, respectively.

256

257 **2.3.1.2 Second irrigation cycle (n=2)**

258 The calculations for the second cycle are essentially the same as those for the first cycle.

259 The main difference concerns the starting point, i.e., the volumetric flow balance at point

260 #0, now given by:

$$261 \quad \Phi_v(1) = \Phi_v(2) + \Phi_v(3) + \Phi_v(5) \quad (8)$$

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

$$263 \quad \Phi_v(1) = \xi_2 \Phi_v(1) + \varepsilon_2 \Phi_v(1) + (1 - \theta) \Phi_v(1) \quad (9)$$

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

$$265 \quad \phi(v, 1) = (\theta - \varepsilon_2) \phi(v, 1) + \varepsilon_2 \phi(v, 1) + (1 - \theta) \phi(v, 1) \quad (10)$$

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

$$267 \quad [K^+]_{0,2} = \xi_2 \Psi + \varepsilon_2 N + (1 - \theta) [K^+]_{2,1} = (\theta - \varepsilon_2) \Psi + \varepsilon_2 N + (1 - \theta) [K^+]_{2,1} \quad (11)$$

$$268 \quad \varepsilon_2 = ([K^+]_{0,2} - (1 - \theta) [K^+]_{2,1} - \theta \Psi) / (N - \Psi) \quad (12)$$

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

$$270 \quad [Na^+]_{0,2} = \varepsilon_2 (M - X) + \theta X + (1 - \theta) [Na^+]_{2,1} \quad (13)$$

$$271 \quad [Na^+]_{1,2} = \frac{[\varepsilon_2 (M - X) + \theta X] + L}{1 - \theta} + [Na^+]_{2,1} \quad (14)$$

$$272 \quad [Na^+]_{2,2} = \frac{(1 - \alpha)}{(1 - \theta)} [\varepsilon_2 (M - X) + \theta X + L] + (1 - \alpha) [Na^+]_{2,1} \quad (15)$$

273 Apart from the fact that  $[K^+]_{0,n}$  remains constant for  $n > 1$  (6.6 mM),  $[K^+]_{1,n}$  and  $[K^+]_{2,n}$  are

274 constant as well having (if assuming  $\beta=0.1$ ) a value of 11.4 and 10.3 mM, respectively. In

275 addition, from the second cycle onwards  $\varepsilon_n$  remains constant as well and independent of

276  $n$ . This can be seen after, first, substituting  $\varepsilon_1$  into  $[K^+]_{2,1}$  followed by substituting  $[K^+]_{2,1}$   
 277 into  $\varepsilon_2$ , resulting in:

$$278 \quad \varepsilon_n = \frac{[K^+]_{0,n}(1-(1-\beta)(1-\mu))-\theta \times \Psi}{N-\Psi} \quad (16)$$

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

281

### 282 2.3.3 Generalized expressions

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

$$294 \quad [Na^+]_{0,n} = (M - X) \sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i}] + (X\theta + L) \sum_{i=1}^{n-2} [(1 - \alpha)^i] + (X +$$

$$295 \quad L)(1 - \alpha)^{(n-1)} + X\theta \quad (17)$$

$$296 \quad [Na^+]_{1,n} = \frac{1}{(1-\theta)} [\sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i}] + [(X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^{(i-1)}] + (1 - \alpha)^{(n-1)} \times$$

$$297 \quad (X + L)] \quad (18)$$

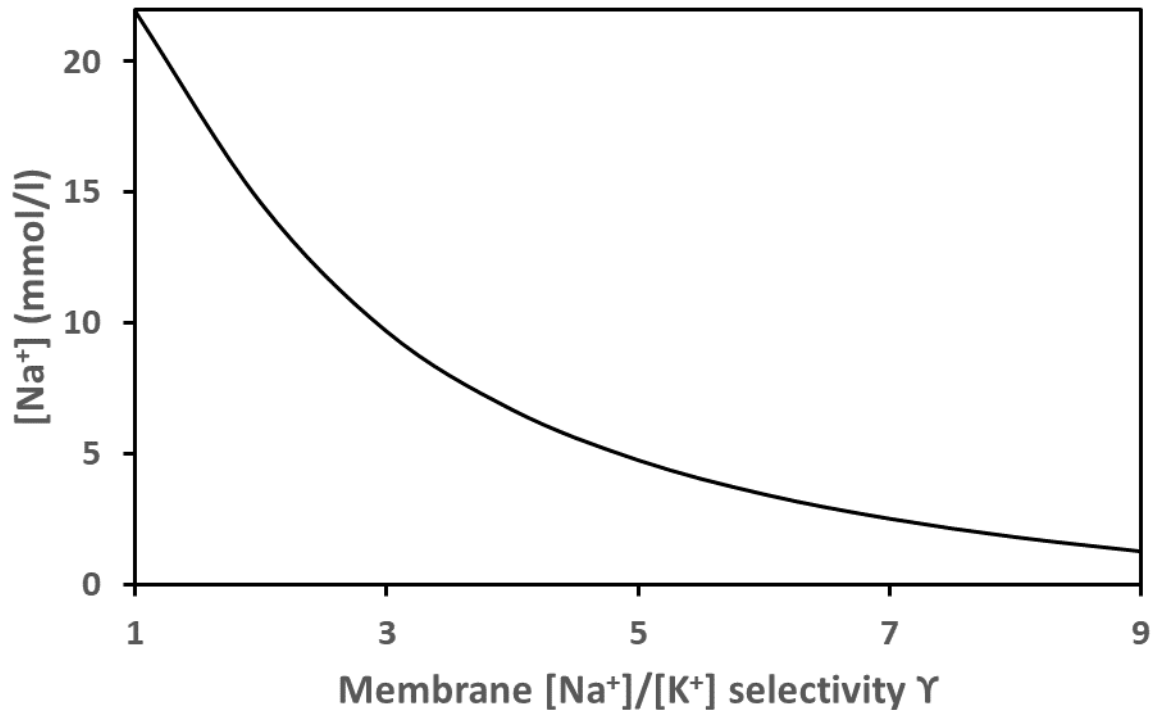
298 Note that for  $n=2$  and after a number of repeated substitutions, Eqs. 17 and 18 reduce to  
299 Eqs. 13 and 14, respectively.

## 300 4. Results and discussion

### 301 4.1 Membrane selectivity

302 The  $\text{Na}^+$  over  $\text{K}^+$  permeation selectivity also is an intrinsic membrane property. As stated  
303 previously, one of our prime goals is to determine the minimum membrane selectivity ( $\gamma$ )  
304 required to maintain the  $\text{Na}^+$  concentration in the IW below the upper tolerance level of  
305 4-5 mM. Because the membrane selectivity ( $\gamma$ ) is defined as the ratio of its permeability  
306 towards  $\text{Na}^+$  ( $\alpha$ ) and its permeability towards  $\text{K}^+$  ( $\beta$ ), the permeation of both ion species  
307 is coupled. With both  $\beta$  and  $\gamma$  set at a fixed value,  $\alpha$  can be calculated and with that the  
308  $\text{Na}^+$  level at point #2, which, in turn, allows the calculation of the  $\text{Na}^+$  level at point #0 at  
309 the start of a new cycle.

310 To compromise between minimizing  $\text{K}^+$  loss and dealing with a finite membrane  
311 selectivity, the value of  $\beta$  is set (arbitrarily) at 0.1, implying that 10% of  $\text{K}^+$  is removed  
312 together with  $\text{Na}^+$ . In combination with a membrane that does not discriminate between  
313  $\text{K}^+$  and  $\text{Na}^+$  ( $\gamma = 1$ ) this results in a  $\text{Na}^+$  removal of also 10%. In this case it is expected to  
314 see a dramatic  $\text{Na}^+$  accumulation in the IW. Figure 3 confirms this expectation showing  
315 the  $\text{Na}^+$  level in the IW after 10 cycles of operation and for a  $\text{Na}^+$  over  $\text{K}^+$  selectivity  
316 ranging from  $\gamma = 1$  to 9. Note that  $\gamma = 1$  indeed results in staggering  $\text{Na}^+$  concentrations  
317 after 10 cycles of operation.



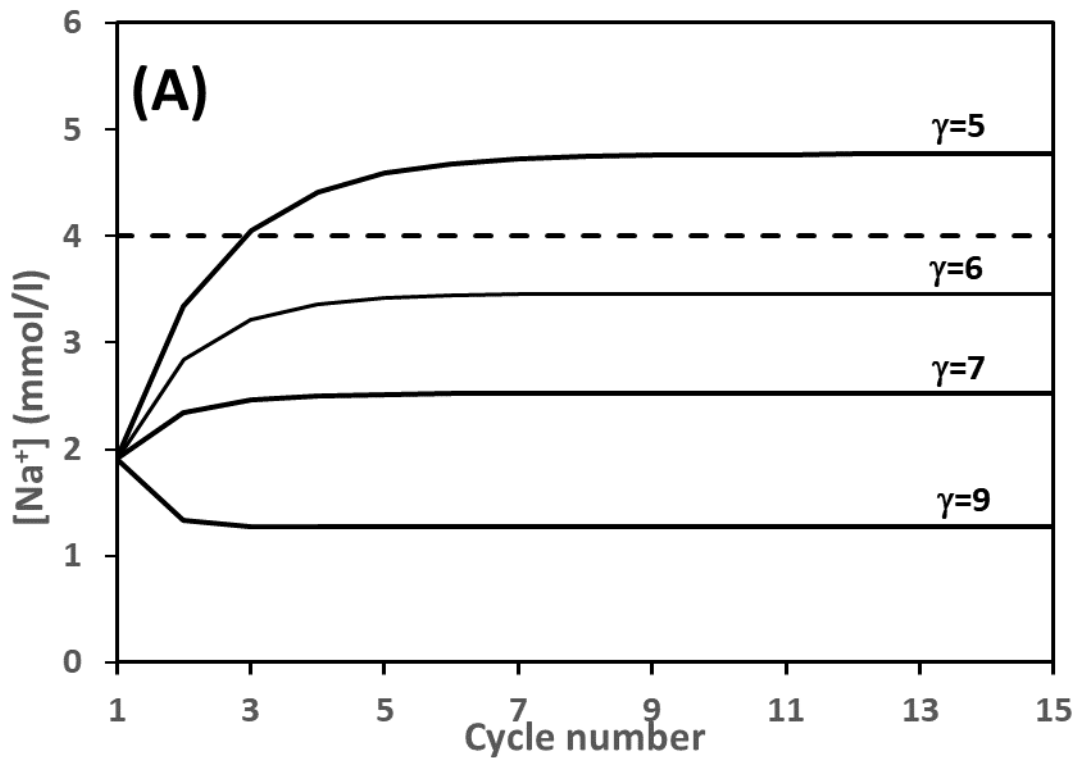
318

319 **Figure 3.** Accumulation of  $\text{Na}^+$  in the irrigation water entering the greenhouse (i.e., at  
 320 point #0) after 10 cycles of operation for a membrane with a  $\text{Na}^+/\text{K}^+$  selectivity ranging  
 321 from 1 to 9 and a  $\text{K}^+$  permeability  $\beta$  of 0.1, i.e., with 10% - 90% of the  $\text{Na}^+$  and 10% of the  
 322  $\text{K}^+$  removed.

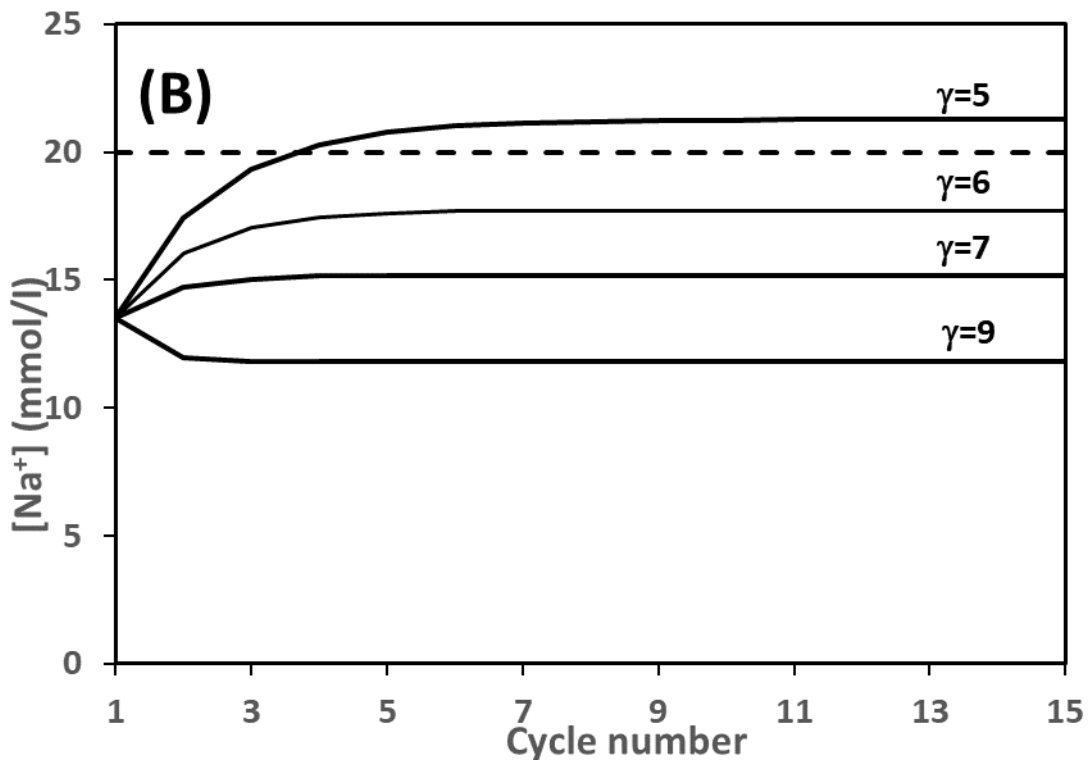
323

324 Figure 4 explores the relationship between membrane selectivity and the  $\text{Na}^+$  level at  
 325 points #0 and #1 during 15 subsequent cycles of operation, given the 10% removal of  $\text{K}^+$   
 326 ( $\beta = 0.1$ ) and for a  $\text{Na}^+$  over  $\text{K}^+$  membrane permeability selectivity ranging from 5 to 9. A  
 327 membrane selectivity of 5 does not suffice to achieve a steady-state  $[\text{Na}^+]$  below the  
 328 threshold of 4 mM at point #0 (A) and of 20 mM at point #1 (B). Indeed, it requires at  
 329 least a selectivity of 6 to accomplish steady-state levels remaining below these  
 330 thresholds. As indicated in Fig. 2,  $\text{Na}^+$  is entering the system from three sources, the  
 331 fresh water, the fertilizer content and the  $\text{Na}^+$  leaching from the coconut-based substrate  
 332 used. As already remarked, from the second cycle on  $\varepsilon_n$  adopts a constant numerical  
 333 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  
 334 amount of  $\text{Na}^+$  entering the system from the fresh water and fertilizer is 3 and 72 g/hr,

335 respectively. The  $\text{Na}^+$  concentration increase due to leaching equals 3.1 mM, resulting in  
336 285 g/hr. Evidently, at steady state the total amount of 360 gr/hr equals the amount of  
337  $\text{Na}^+$  that needs to be removed by the membrane unit.



338



339

340 **Figure 4.** (A).  $[Na^+]$  in the irrigation water entering the greenhouse at point #0; (B).  $[Na^+]$   
 341 in the irrigation water leaving the greenhouse at point #1 during 15 cycles of operation,  
 342 for a  $Na^+/K^+$  membrane selectivity ranging from 5 to 9 and a  $K^+$  permeability  $\beta$  of 0.1,  
 343 i.e., with 50% - 90% of the  $Na^+$  and 10% of the  $K^+$  removed. Dotted lines represent the  
 344 threshold of 4 mM of the  $Na^+$  content of the IW entering the greenhouse (A) and the  
 345 physiological tolerance threshold for tomato of 20 mM (B).

346



347 In order to maintain a steady-state  $K^+$  concentration in the IW of 6.6 mM, the added  
348 amount of  $K^+$ , originating from the fertilizer, equals  $\varepsilon_n \times N \times \Phi_v(1) = 430$  g/hr.

349

### 350 **4.3 Implementation**

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

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

$$362 \quad A = Q \times F \times ([Na^+]_{1,2} - [Na^+]_{2,2}) / if \quad (19)$$

363 The volumetric flow  $Q$  equals  $\Phi_v(4) = 0.37 \times \Phi_v(1) = 4.1 \times 10^{-4} \text{ m}^3/s$ . As mentioned  
364 before, any water flow arising from either osmosis or electro osmosis is ignored, given  
365 the strong hydrophobic nature of the LSM system. According to Fig. 2 and given  $\alpha=0.6$   
366 and  $\beta=0.1$  (Fig. 4A with  $\gamma=6$ ),  $[Na^+]_{0,n}$  reaches a steady-state value of 3.45 mM. The  
367 difference between the  $Na^+$  concentration of the solution entering and leaving the  
368 membrane then is  $0.6 \times (3.5 + 3.1) / 0.37 = 10.7$  mM. Note that this concentration difference  
369 results in  $10.7 \times 10^{-3} \times 23 \times 4000 \times 0.37 = 365$  gr  $Na^+$ /hr that needs to be removed, essentially  
370 the same amount as previously derived from the amount of  $Na^+$  entering the system. As

371 for the current density, we take a 'typical' value for ion exchange membranes given a  
372 total ionic strength of the incoming water of around 25-30 mM, i.e., 10 A/m<sup>2</sup> [23].  
373 Further, as a rather conservative estimate the current utilization factor ( $f$ ) is assumed to  
374 be 0.6, implying that 60% of the current is actually carried by Na<sup>+</sup>, the remaining 40% by  
375 K<sup>+</sup> and other ion species present. Substituting these numbers in Eq. 19 renders a  
376 membrane surface area of 70 m<sup>2</sup>. In practice, this could be achieved by constructing ED  
377 stacks with a number of cells in series. For instance, three ED modules, each comprising  
378 of a stack of 12 cells with a membrane surface area of 2 m<sup>2</sup> each.

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

### 388 **4.3 Economics perspective**

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

393 Firstly, the capital cost of the LSM currently developed and validated is to a large extent  
394 dominated by the amount of 15-crown-5 needed. When purchased from TCI-Chemicals

395 and given the 15-crown-5 density (0.2 M), the membrane thickness (100  $\mu\text{m}$ ) and a  
396 support porosity of 50% the estimated cost price amounts to 78 euro per  $\text{m}^2$ . To put this  
397 number in perspective, the price of typical commercially available ion exchange  
398 membranes is around 30 euro per  $\text{m}^2$ . The most promising options to bring the price  
399 from the LSM down, seem a thinner membrane and upscaling 15-crown-5 (in-house)  
400 synthesis. It should be mentioned however that the (at this moment unknown and  
401 therefore not considered here) manufacturing cost contribute significantly to if not  
402 dominate the cost prize (Fuji Film, Netherlands; personal communication).

403 Secondly, the operational costs on the other hand will be dominated by the power  
404 needed to run the system. Based on the specifications of a typical ED system and given  
405 the salt concentration in the feed, the power consumption will be in the range 0.7 – 2.5  
406  $\text{kWh/m}^3$  [24]. The power consumption is linear with the applied current density [22]  
407 and as evident from Eq. 19, there are essentially three ways to reduce the required total  
408 membrane surface area: by reducing the volumetric flow through the system, by  
409 increasing the current utilization factor or by increasing the current density. Reduction  
410 of the volumetric flow could (possibly) be accomplished by a different configuration  
411 altogether. For instance, by positioning the membrane module not in the main stream  
412 (as in Figs. 1, 2) but instead in a bypass. This option will be explored in more detail once  
413 we (experimentally) obtained the actual specifications of our membrane under  
414 development. Improving the current utilization factor implies a higher  $\text{Na}^+$  over  $\text{K}^+$   
415 membrane selectivity. Even though the cost for re-supplementing the IW with  $\text{K}^+$  will go  
416 down, the membrane itself will (probably) be more expensive due to the higher density  
417 of crown ethers required. Finally, a higher current density will reduce the total  
418 membrane surface area needed but increase the power needed during operation. As  
419 pointed out by Strathmann [22], the opposite effect of current density on required

420 membrane surface area and energy cost may translate in an optimal current density,  
421 resulting in the lowest overall costs.

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

## 428 **5. Conclusion**

429 Excess Na<sup>+</sup> in irrigation water needs to be removed to a level dictated by the tolerance  
430 threshold specific for the particular crop, for tomato 20 mM. The closed-loop irrigation  
431 water system described here includes a membrane-based module to remove excess Na<sup>+</sup>  
432 while preserving the (nutrient) K<sup>+</sup> as much as possible. Based on real-life process  
433 parameters, the present study indicates that a Na<sup>+</sup> over K<sup>+</sup> membrane permeation  
434 selectivity of 6 already suffices to remain the Na<sup>+</sup> level the plants are exposed to below  
435 20 mM, at least if accepted that 10% of the K<sup>+</sup> is removed as well. If implemented in an  
436 electro dialysis set-up while assuming a constant current density of 10 A/m<sup>2</sup>, the  
437 estimated total membrane surface is 70 m<sup>2</sup>. Considering the opposite effect of current  
438 density on required membrane surface area and energy cost, an optimum current  
439 density is hypothesized, resulting in a minimum of overall cost.

## 440 **Conflict of Interest Statement**

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

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521

522 **Supporting information**

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

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526 As in the manuscript, the nomenclature practiced is based on the use of two indices, the  
527 first representing the reference point, the second the cycle number. For instance, [Na<sup>+</sup>]<sub>2,3</sub>  
528 refers to the Na<sup>+</sup> concentration at point #2 during the third cycle.

529 The manuscript gives the equations for  $\varepsilon$  and the K<sup>+</sup> and Na<sup>+</sup> concentrations during the  
530 1<sup>st</sup> and 2<sup>nd</sup> cycle of operation. Here the expressions for the Na<sup>+</sup> concentrations at the  
531 three reference points during the 2<sup>nd</sup> cycle are given again but, in contrast to the  
532 manuscript, this time exclusively in terms of known parameters, as required to derive  
533 the generalized expressions.

534  $[\text{Na}^+]_{0,2} = (M - X)[\varepsilon_2 + \varepsilon_1(1 - \alpha)] + (X + L)(1 - \alpha) + \Theta X$   
535 (1)

536  $[\text{Na}^+]_{1,2} = [(M - X)[\varepsilon_2 + \varepsilon_1(1 - \alpha)] + (X + L)(1 - \alpha) + \Theta X + L]/(1 - \theta)$   
537 (2)

538  $[\text{Na}^+]_{2,2} =$   
539  $[(M - X)[\varepsilon_2(1 - \alpha) + \varepsilon_1(1 - \alpha)^2] + (X + L)(1 - \alpha)^2 + (\Theta X + L)(1 - \alpha)]/(1 - \theta)$   
540 (3)

541 As shown in the manuscript (Eq. 16), from the 2<sup>nd</sup> cycle on  $\varepsilon_n$  becomes constant:

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

543

544 Apart from the fact that [K<sup>+</sup>]<sub>0,n</sub> remains constant for n>1 (6.6 mM), [K<sup>+</sup>]<sub>1,n</sub> and [K<sup>+</sup>]<sub>2,n</sub> are  
545 constant as well having (if assuming  $\beta=0.1$ ) a value of 11.4 and 10.3 mM, respectively.  
546 For this reason, this Supplement is restricted to the Na<sup>+</sup> level at each reference point for  
547 n>2.

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

549 ***Reference point #0***

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

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

551  
552 (5)

553 **Reference point #1**

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

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

555  
556 (6)

557

558 **Reference point #2**

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

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

560  
561 (7)

562

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

564 **Reference point #0**

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

565  
566 (8)

567 **Reference point #1**

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

568  
569 (9)

570 **Reference point #2**

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

571  
572 (10)



573

574

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

576 ***Reference point #0***

577 
$$[\text{Na}^+]_{0,5} = (M - X) \times [\varepsilon_5 + \varepsilon_4(1 - \alpha) + \varepsilon_3(1 - \alpha)^2 + \varepsilon_2(1 - \alpha)^3 + \varepsilon_1(1 - \alpha)^4] +$$
  
578 
$$(1 - \alpha)^4(X + L) + (1 - \alpha)^3(X\theta + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta$$
  
579 (11)

580

581 ***Reference point #1***

582 
$$[\text{Na}^+]_{1,5} = [(M - X) \times [\varepsilon_5 + \varepsilon_4(1 - \alpha) + \varepsilon_3(1 - \alpha)^2 + \varepsilon_2(1 - \alpha)^3 + \varepsilon_1(1 - \alpha)^4] +$$
  
583 
$$(1 - \alpha)^4(X + L) + (1 - \alpha)^3(X\theta + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta +$$
  
$$L]/(1 - \theta)$$
  
(12)

584 ***Reference point #2***

585 
$$[\text{Na}^+]_{2,5} = [(M - X) \times [\varepsilon_5(1 - \alpha) + \varepsilon_4(1 - \alpha)^2 + \varepsilon_3(1 - \alpha)^3 + \varepsilon_2(1 - \alpha)^4 +$$
  
586 
$$\varepsilon_1(1 - \alpha)^5] + (1 - \alpha)^5(X + L) + (1 - \alpha)^4(X\theta + L) + (1 - \alpha)^3(X\theta + L) +$$
  
$$(1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L)]/(1 - \theta)$$
  
(13)

587 **Generalized expressions for the n<sup>th</sup> irrigation cycle (n≥2)**

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

591 
$$[\text{Na}^+]_{0,n} = (M - X) \sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i}] + (X\theta + L) \sum_{i=1}^{n-2} [(1 - \alpha)^i] + (X + L) \times$$
  
592 
$$(1 - \alpha)^{(n-1)} + X\theta$$
  
(14)

593 Using the generalized form of Eq. 7 in the manuscript:

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

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

596 
$$[\text{Na}^+]_{1,n} = \frac{1}{(1-\theta)} [(M - X) \sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i}] + [(X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^{(i-1)}] +$$
  
 597  $(1 - \alpha)^{(n-1)} \times (X + L)]$   
 (15)

598

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

600

601 
$$[\text{Na}^+]_{1,n} = \frac{1}{(1-\theta)} [(M - X) \sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i+1}] + [(X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^i] +$$
  
 602  $(1 - \alpha)^n \times (X + L)]$   
 (16)

603

604

Figure 1

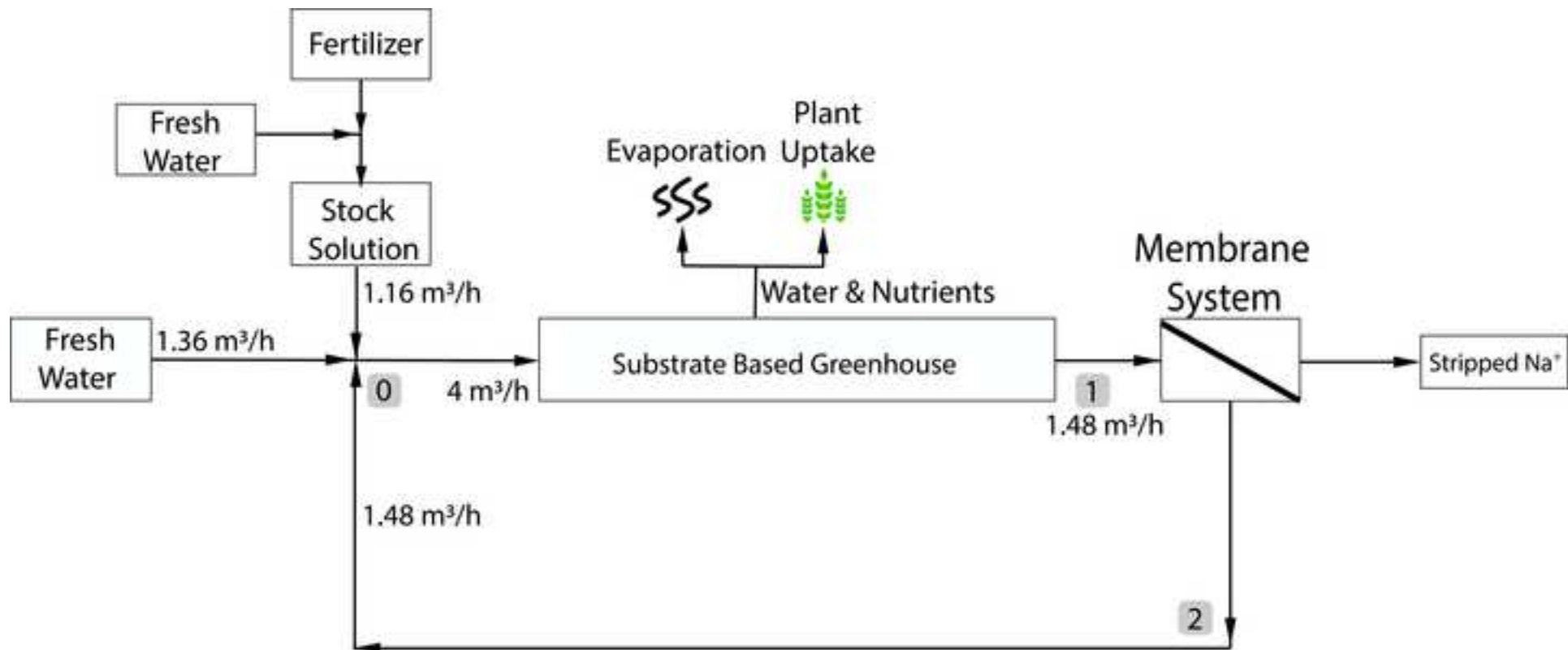


Figure 2

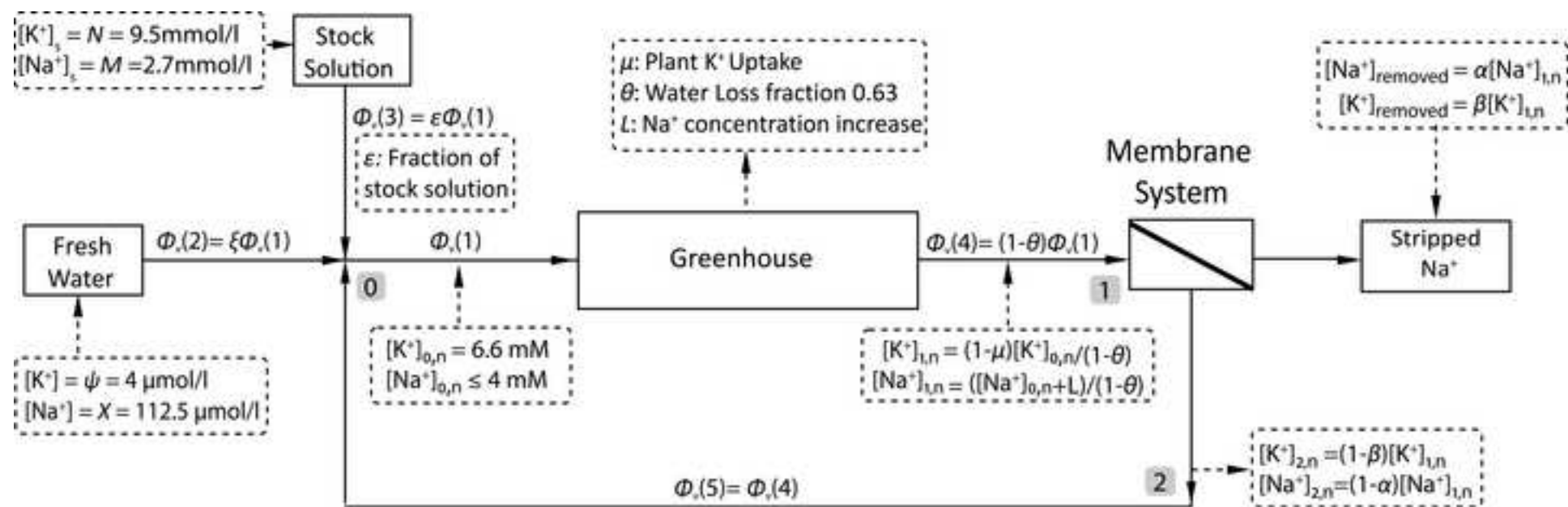


Figure 3

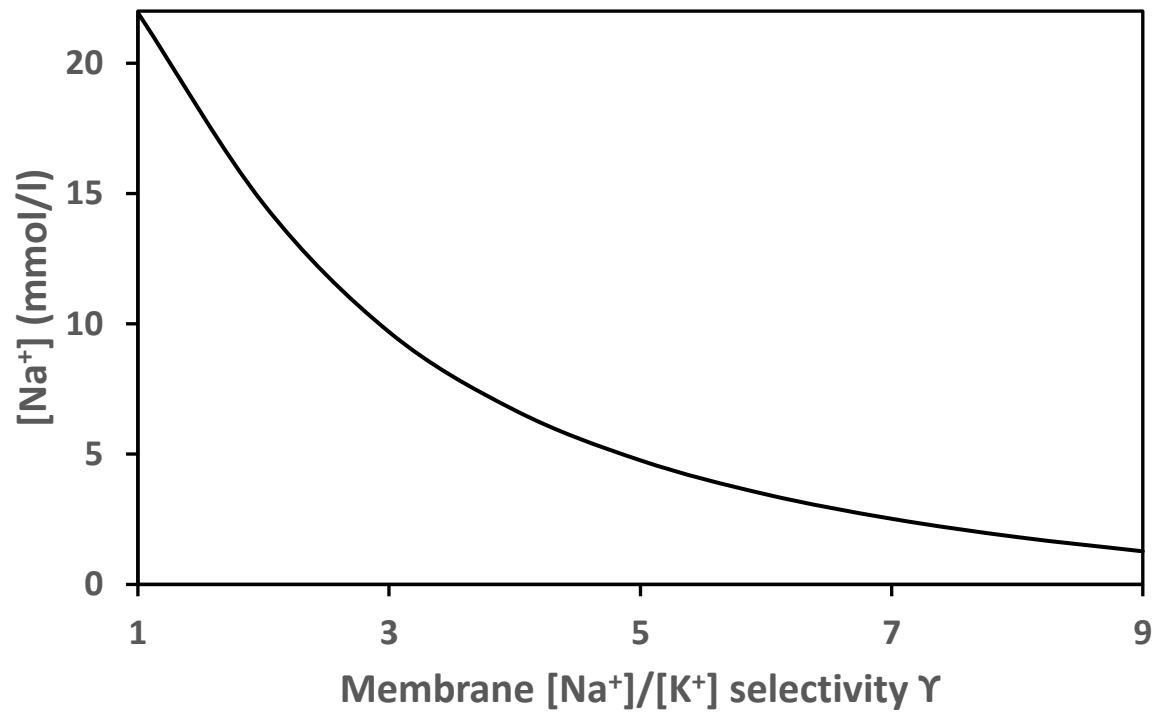
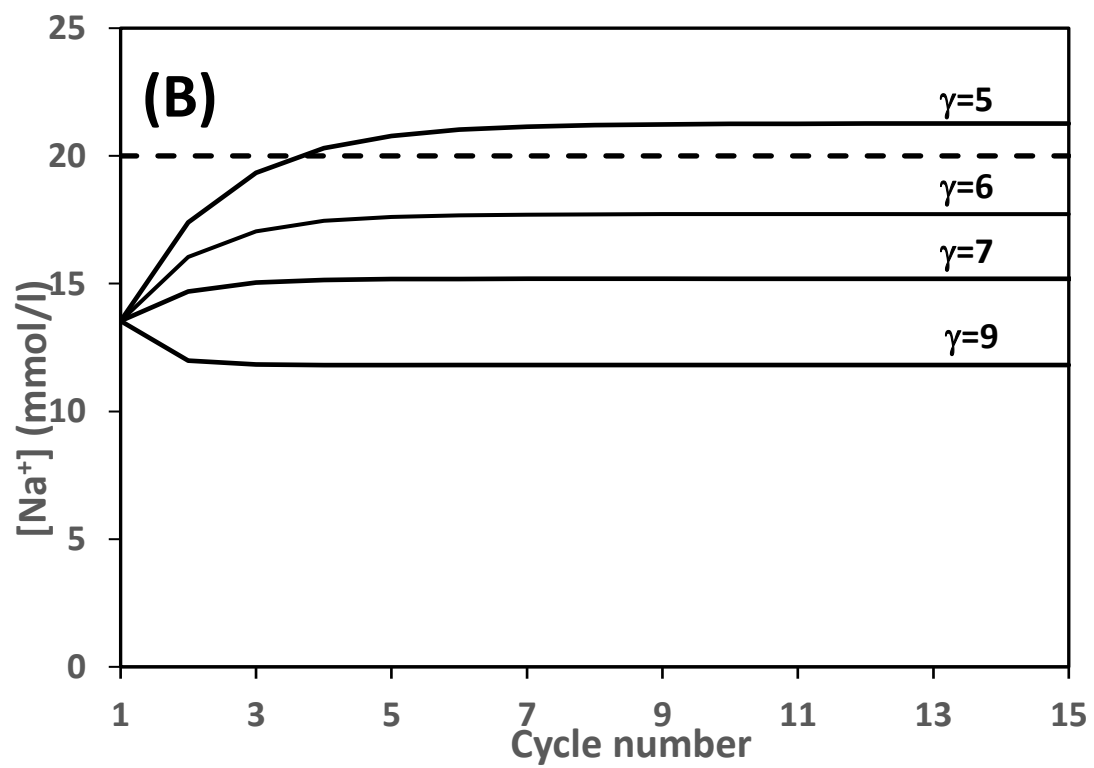
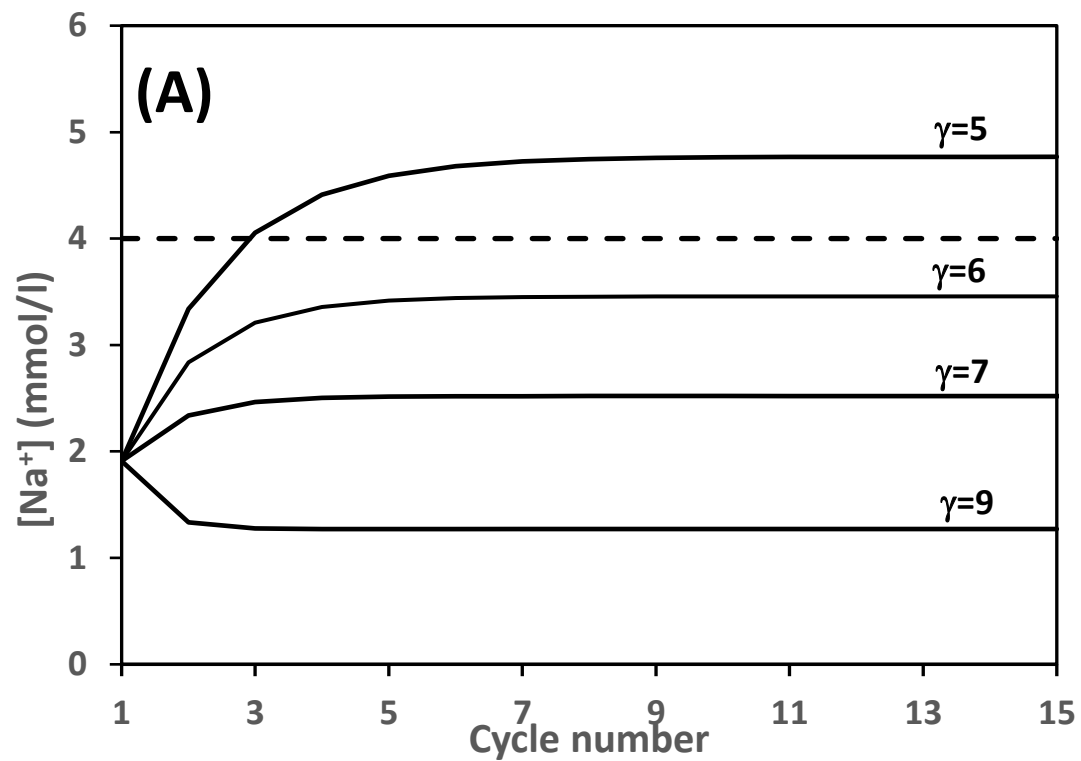


Figure 4



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

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