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

Leeuwarden, March 2nd, 2018

Dear Editor,

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

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

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

Sincerely,

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Point-by-point reply to the reviewers' reports

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

Reviewer: 1

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

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

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

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

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

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

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

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

Reviewer: 2

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

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

1. Not much recent literature is referred to; only 2 references more recent than 2010. Membrane separations is an active field, developments are fast!

>>We fully agree and address this issue in lines 61-78. Additional remarks but in a slightly different context can be found in lines 173 - 178 and 393 - 402. We also added references 13-21 regarding membrane technology, with 5 out of 9 published in 2016 or later (see also point #3 of Reviewer 1).

2. It seems that the actual problem is the high Na content in the fertilizer (line 104) - can't that be improved?

>>This remark made us reconsider the sources of Na+ entry. We added a calculation of the amount of Na+ entering the system, see lines 330 - 337. As can be concluded from this calculation, the leaching from the substrate contributes most to the amount of Na+ entering the IW system. So even if the Na+ content of the fertilizer could be drastically reduced, Na+ still accumulates in the (recycled) IW but at a lower rate. See also lines 351 – 354.

3. Also, it may be a good / better idea to lower the Na+ content of the rainwater used, using a reverse osmosis membrane process.

>>Please see the comment on the previous question.

4. line 51: similar size.... well I would say that the larger size of K+ is a key to separate it from smaller Na+. For example using a zeolite...

>>The Reviewer is absolutely correct that certain zeolites do indeed show sieve properties and do distinguish between cations of different size. However, those applications refer to absorbance- rather than membrane-based technology. Our aim is to go for the latter because in this way the inevitable regeneration step of the resin after it has been saturated with Na+ is avoided, see lines 57 – 60.

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

6. line 117: zero water transportation through the membrane ?? I mistake I guess; water will go through the membrane carrying the Na+, K+ ions....

>>The very hydrophobic nature of the Liquid Supported Membrane (LSM) we currently develop implies an essentially zero water permeation. This issued is addressed in lines 173 – 178.

7. line 126-131: so the concentration K+ increases from 6.6 to 11.4 mM in the greenhouse "process" - but that is more than the 6.6 mM that the plants want?

>>*The Reviewer is absolutely right, as formulated this statement was prone to misunderstanding and confusion. The optimal K⁺ concentration of 6.6 mM (advised by our 'greenhouse and fertilizer' partners van der Knaap and Yara) refers to the K⁺ content of the incoming water (i.e., at point #0 in Figs. 1 and 2). This is now clearly explained in lines 126 – 129 (and again mentioned in lines 150 – 152).*

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

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

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

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

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

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

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

11. line 195 typo uses -- used.

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

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

>>*We double checked all equations and actually did find a small mistake in the expression for the Na⁺ content of the water leaving the greenhouse. Even though the story remains essentially the same, the data shown in Figs. 3 and 4 slightly changed, as well as the*

conclusion that given a 10% loss of K+, a Na+ over K+ permeation selectivity of 6 suffices (instead of 7 previously).

In addition, we explicitly state that the generalized expressions 17 and 18 can be reduced to Eqs. 13 and 14 (lines 298 – 299). The calculations for Figs. 3 and 4 were performed both ways, first, from cycle to cycle and, secondly, using the generalized Eqs. 17 and 18. Either way, the results were the same.

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

>>Point taken from the Reviewer, this part has been taken out completely.

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

>>Point taken from the Reviewer, this part has been taken out completely.

15. line 366: and what is the value for Na+ added?

>>The Na+ entering the system from different sources is now explained in lines 330 – 337. See also question #2 of this Reviewer.

16. figure 5: add lines for gamma values 7,8,9. There it becomes interesting / useful for the reader, for an acceptable ChERD paper.

>>We fully agree, this substantially clarifies the figure.

17. page 19-20: do membranes exist that can give the properties needed?

>>There are no currently existing separation (i.e., for high fluxes) membranes that can discriminate between two ion species of equal valance. This information has been added to the text (lines 61 – 71), as well as the type of membrane we aim for (lines 72 – 78 and lines 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 m³ processed (fed to the membrane)

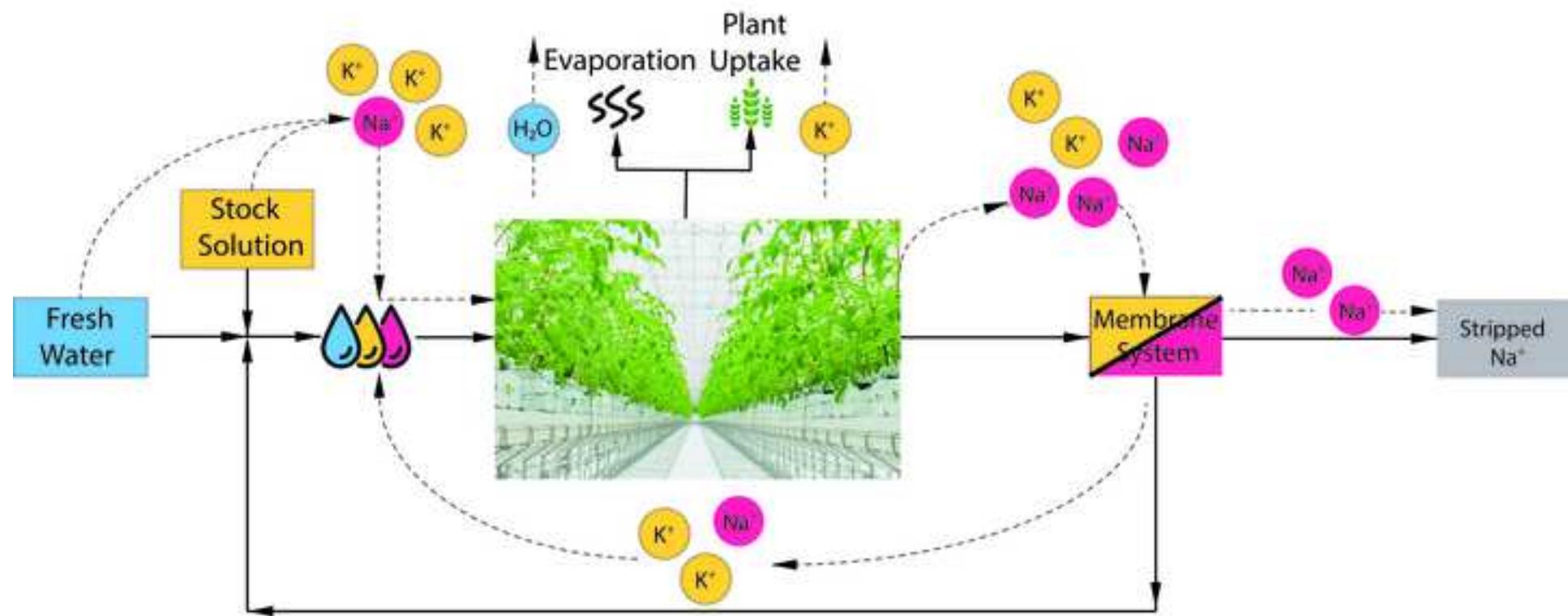
>>Even though it remains an intelligent guess rather than an accurate prediction, we thank the Reviewer for this valuable suggestion and agree to pay more attention to this issue. Capital costs are discussed in lines 393 – 402 and 417 – 421 and power consumption in lines 355 – 378 and 403 – 421.

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⁺ content, should be considered too.

>>As argued, the Na⁺ concentration increase due to leaching equals 285 g/hr, far more than the Na⁺ entering the system from the fresh water and fertilizer, 3 and 72 g/hr, respectively. See lines 351 – 354 and question #2 of this Reviewer.



- Simulation of Na⁺ and K⁺ concentration in recycled closed-loop irrigation water.
- Development of a membrane-based system for the removal of excess Na⁺.
- Permeation selectivity of 6 suffices to maintain the system under Na⁺ threshold.
- Implementation of an electro-dialysis like set-up.
- Required membrane surface area around 70 m².

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⁺ and K⁺ 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⁺ but includes a membrane unit for
15 the selective removal of Na⁺ as well. As determined by the membrane properties, some
16 of the K⁺ is removed as well. Based on real-life process parameters, the model calculates
17 the Na⁺ and K⁺ concentration at three reference points. These process parameters
18 include the evapotranspiration rate, the K⁺ uptake by the plants, the Na⁺ and K⁺ content
19 of the fertilizer, the Na⁺ leaching out from the hydroponic substrate material, and the
20 Na⁺ and K⁺ removal efficiency of the membrane unit. Using these parameters and given a
21 constant K⁺ concentration of the irrigation water entering the greenhouse of 6.6 mM
22 (resulting in the optimal K⁺ 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 Na⁺ over K⁺
26 selectivity of 6, after a number of cycles the 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; Na⁺ over 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. Na⁺
40 is a typical example of an ion that over time builds up in the IW [2]. High 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 Na⁺, the IW 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 Na⁺ level in the IW during crop growth.
45 Despite the detrimental effects at higher levels, plants do show a certain tolerance for
46 Na⁺. Reported 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 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 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 Na^+ from the IW. A complication arises
53 from the fact that K^+ , an essential plant nutrient, has very similar physicochemical
54 properties as 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 Na^+ and K^+ , respectively.
56 However, a key (physiological) difference between the two ion species is that Na^+ is
57 hardly taken up by the plant and is the major cause of salinity toxicity [11, 12]. Excess
58 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 Na^+ .

61 The fact that Na^+ and 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 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⁺ 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⁺ 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.

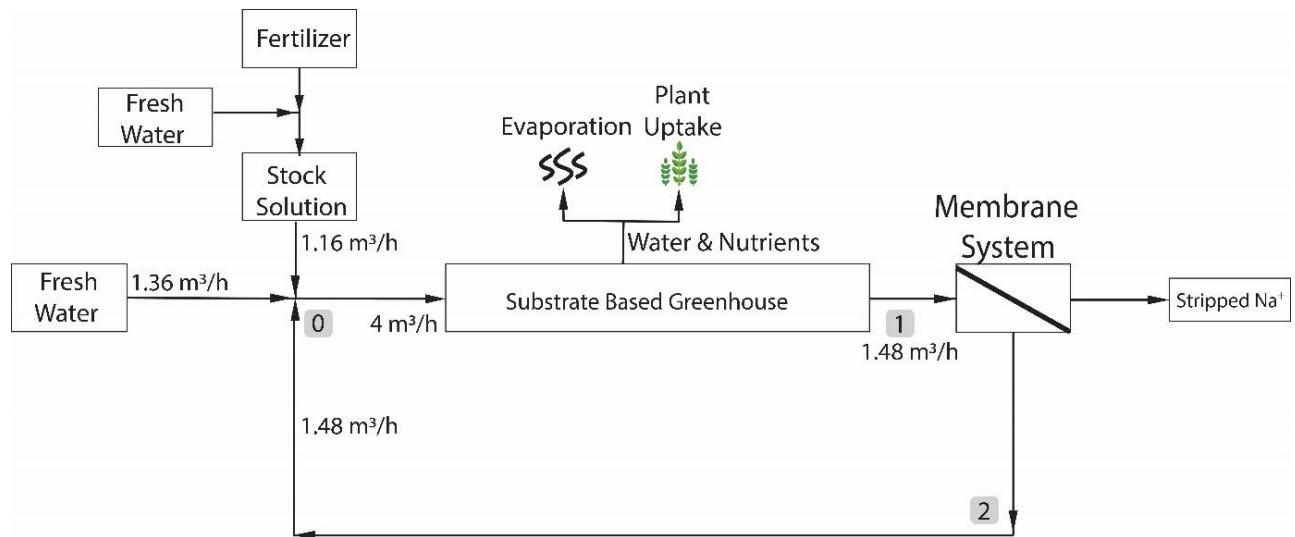
79 The technological challenge thus is to develop a separation membrane that permeates
80 Na⁺ but not, or at least to a much lower extent, K⁺. Obviously, the less permeable for K⁺,
81 the less K⁺ needs to be re-supplied to compensate for this loss. Therefore, a key question
82 for the membrane-to-be-developed concerns its required Na⁺ over K⁺ permeation
83 selectivity. Crucial here to realize is that there is no need to remove all Na⁺. Instead, all
84 that needs to be achieved is a (steady-state) concentration of Na⁺ below the threshold
85 for, in this case, tomato cultivation. Apart from the fact that total Na⁺ 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⁺ re-supply and, even more 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⁺ over K⁺ permeation selectivity and K⁺
91 and Na⁺ permeability and flux, given real-life operational process parameters (e.g., K⁺
92 uptake by tomato, optimal K⁺ level in the IW, evapotranspiration). The simulation study
93 presented here is based on the calculation of the K⁺ and Na⁺ 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^+ 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^+ uptake by the tomato plants and evapotranspiration, the optimal K^+
128 concentration of the IW entering the greenhouse is 6.6 mM whereas the (detrimental)
129 threshold Na^+ 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^+ and 2.7 mM Na^+ (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^+ and Na^+ 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⁺ and Na⁺ 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⁺ and Na⁺,
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⁺ concentration.* K⁺ enters the system from two potential sources:

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

148 Furthermore, K⁺ leaves the system at two locations. Firstly, the nutritional K⁺ uptake by
149 the crops and, secondly, the loss through the membrane unit due to the given Na⁺ over
150 K⁺ permeation selectivity of the membrane. Given the optimal K⁺ 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⁺ uptake
153 by the plants (μ) has been determined experimentally by measuring the K⁺
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⁺ entering the
156 greenhouse (6.6 mM):

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

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

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

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

163 Because 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 Na⁺ concentration in the irrigation water
165 is 1.9 mM (resulting from the background Na⁺ concentrations in both fresh water and
166 fertilizer and fixing the K⁺ concentration at point #0 at 6.6 mM). The Na⁺ leaching from
167 the substrate was determined by measuring the 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 Na⁺ is washed out the substrate, the present study
170 assumes a constant degree of leaching during the consecutive cycles of operation.

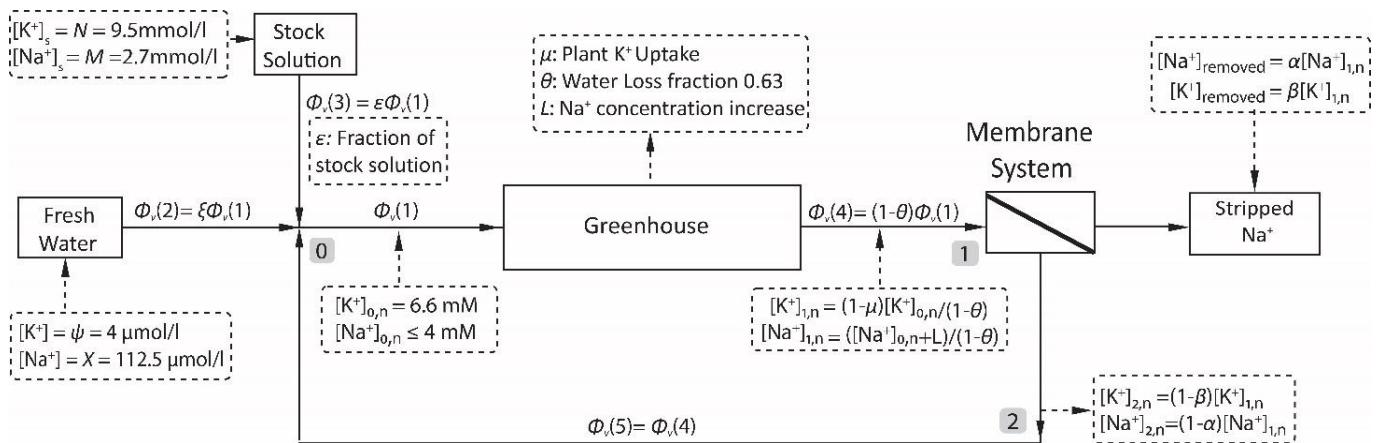
171 The membrane unit needs to remove Na⁺ to meet a (steady-state) Na⁺ concentration
172 level in the irrigation water <20 mM, i.e., the upper tolerance level for Na⁺ of tomato
173 cultivation. Noteworthy, the model assumes that the membrane unit does not remove
174 any water. The reason is that the LSM under development is composed of a hydrophobic
175 support impregnated with a hydrophobic solvent containing the Na⁺ selective carrier 15-
176 crown-5. Prior to entering this organic phase, ions need to be dehydrated with the free
177 energy (ΔG) of dehydration (>0) is compensated for by the ΔG 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⁺
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 (ε)
 189 added at point #0. For that reason, we designated ε the master variable in our
 190 simulations. On the same token, K^+ is the master ionic species, dictating, by means of ε ,
 191 the concentration of the slave ionic species Na^+ at point #0 at the start of each new cycle.
 192 Once ε 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
Ψ	K^+ concentration in fresh water
X	Na^+ concentration in fresh water
N	K^+ concentration in fertilizer stock solution
M	Na^+ concentration in fertilizer stock solution
ξ	fraction of fresh water added at point #0
ε	fraction of fertilizer stock solution added at point #0
μ	fraction of K^+ entering the greenhouse taken up by the crop
L	Na^+ concentration increase due to Na^+ leaching out from the coconut-based substrate
θ	fraction of $\Phi_v(1)$ lost due to evapotranspiration
α	fraction of Na^+ removed from the drain water leaving the greenhouse
β	fraction of K^+ removed from the drain water leaving the greenhouse
γ	Na^+ over K^+ permeation selectivity of the membrane unit

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

209 Volumetric flows (Φ_v) are presented as fraction of the flow entering the greenhouse,
 210 $\Phi_v(1)$ with ε the fraction of the stock solution and ξ 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⁺ concentration for tomato and taken into account K⁺
217 uptake and evapotranspiration, the K⁺ concentration at point #0 is set at 6.6 mM. The
218 Na⁺ threshold of 20 mM is the maximum acceptable Na⁺ level of the IW leaving the
219 greenhouse. Given the Na⁺ leaching out the substrate (3.1 mM) and the
220 evapotranspiration (0.67), the 20 mM translates into a Na⁺ of the IW entering the
221 greenhouse of 20x0.37-3.1=4.3 mM. Throughout this study the threshold Na⁺ level at
222 point #0 of the incoming IW is set at 4 mM.

223 The volumetric flow balance reads:

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

225 Suppose Ψ and N are the K⁺ concentration in the fresh water and in the fertilizer stock
226 solution, respectively. Then, according to Eq. 1, the K⁺ mass balance equals:

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

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

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

230 The fraction of stock solution thus is:

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

232 With $[K^+]_{0,1} = 6.6\text{ mM}$ and Ψ and N being known, the value of ε_1 is defined.

233 Once ε_1 is known, the Na⁺ concentration for the first cycle can be calculated by:

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

235 where M and X are the Na^+ concentration of the stock solution and fresh water,
236 respectively.

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

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

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

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

247

248 **Reference point #2**

249 Reference point #2 is located downstream the membrane unit (permeate side) and
250 calculation of the K^+ and Na^+ concentration at this point therefore requires
251 implementation of the membrane characteristics. Let α be the fraction of Na^+ (compared
252 to reference point #1) that permeates the membrane (and with that removed from the
253 system) and β the fraction of K^+ that permeates the membrane (also removed from the
254 system). Then the K^+ and Na^+ concentrations are given by $[\text{K}^+]_{2,1} = (1 - \theta)[\text{K}^+]_{1,1}$ and
255 $[\text{Na}^+]_{2,1} = (1 - \alpha)[\text{Na}^+]_{1,1}$, 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:

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

266 In analogy with Eq. 2, Eq. 10 results in a K⁺ concentration and ε_2 at point #0 of:

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

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

Once ε_2 has been determined, $[\text{Na}^+]$ at each point can be calculated:

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

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

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

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

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

addition, from the second cycle onwards ε_n remains constant as well and independent of

276 n . This can be seen after, first, substituting ε_1 into $[K^+]_{2,1}$ followed by substituting $[K^+]_{2,1}$
 277 into ε_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, ε_n adopts a numerical value expressed in
 280 terms of β 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 ε and by implication the $[K^+]$ and $[Na^+]$ as
 284 well can all be expressed exclusively in terms of the known process parameters $[K^+]_{0,1}$, α ,
 285 β , μ , θ , r , N , M , X and Ψ . 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 2nd cycle
 293 on are given below (for their derivation, see Supplementary Information).

$$294 \quad [Na^+]_{0,n} = (M - X) \sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i}] + (X\theta + L) \sum_{i=1}^{n-2} [(1 - \alpha)^i] + (X + L)(1 - \alpha)^{(n-1)} + X\theta \\ 295 \quad (17)$$

$$296 \quad [Na^+]_{1,n} = \frac{1}{(1-\theta)} [\sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i}] + [(X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^{(i-1)}]] + (1 - \alpha)^{(n-1)} \times \\ 297 \quad (X + L)] \quad (18)$$

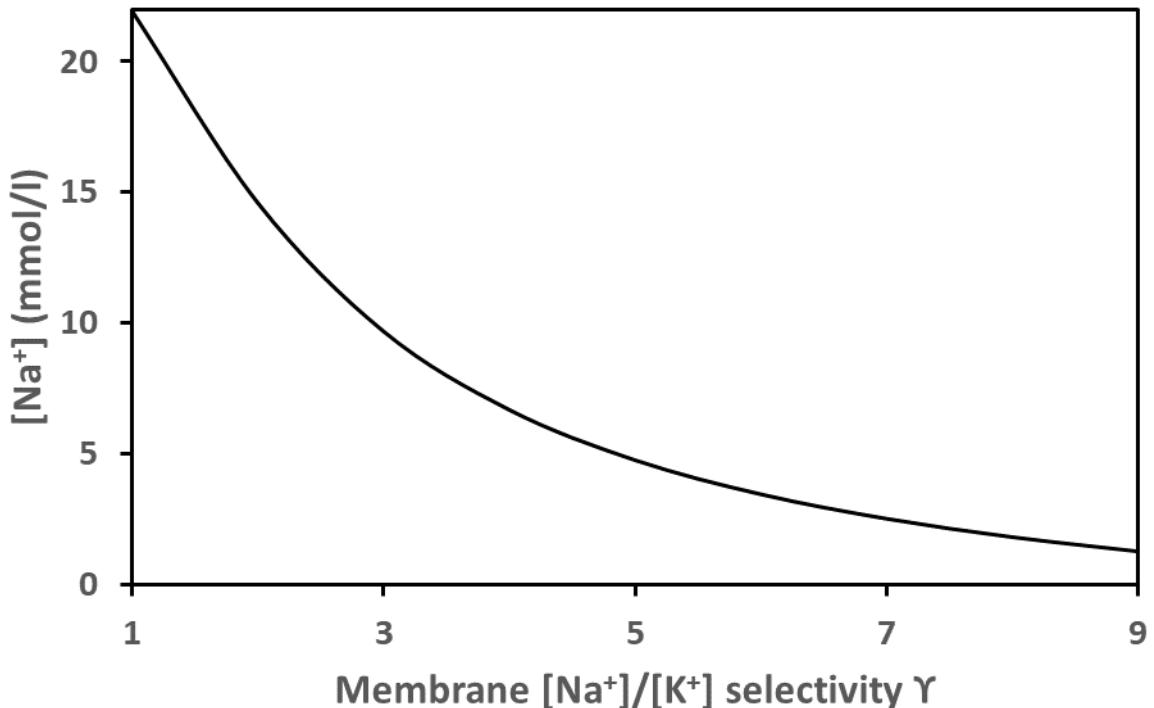
298 Note that for $n=2$ and after a number of repeated substitutions, Eqs. 17 and 18 reduce to
299 Eqs. 13 and 14, respectively.

300 **4. Results and discussion**

301 **4.1 Membrane selectivity**

302 The Na^+ over 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 (γ)
304 required to maintain the Na^+ concentration in the IW below the upper tolerance level of
305 4-5 mM. Because the membrane selectivity (γ) is defined as the ratio of its permeability
306 towards Na^+ (α) and its permeability towards K^+ (β), the permeation of both ion species
307 is coupled. With both β and γ set at a fixed value, α can be calculated and with that the
308 Na^+ level at point #2, which, in turn, allows the calculation of the Na^+ level at point #0 at
309 the start of a new cycle.

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



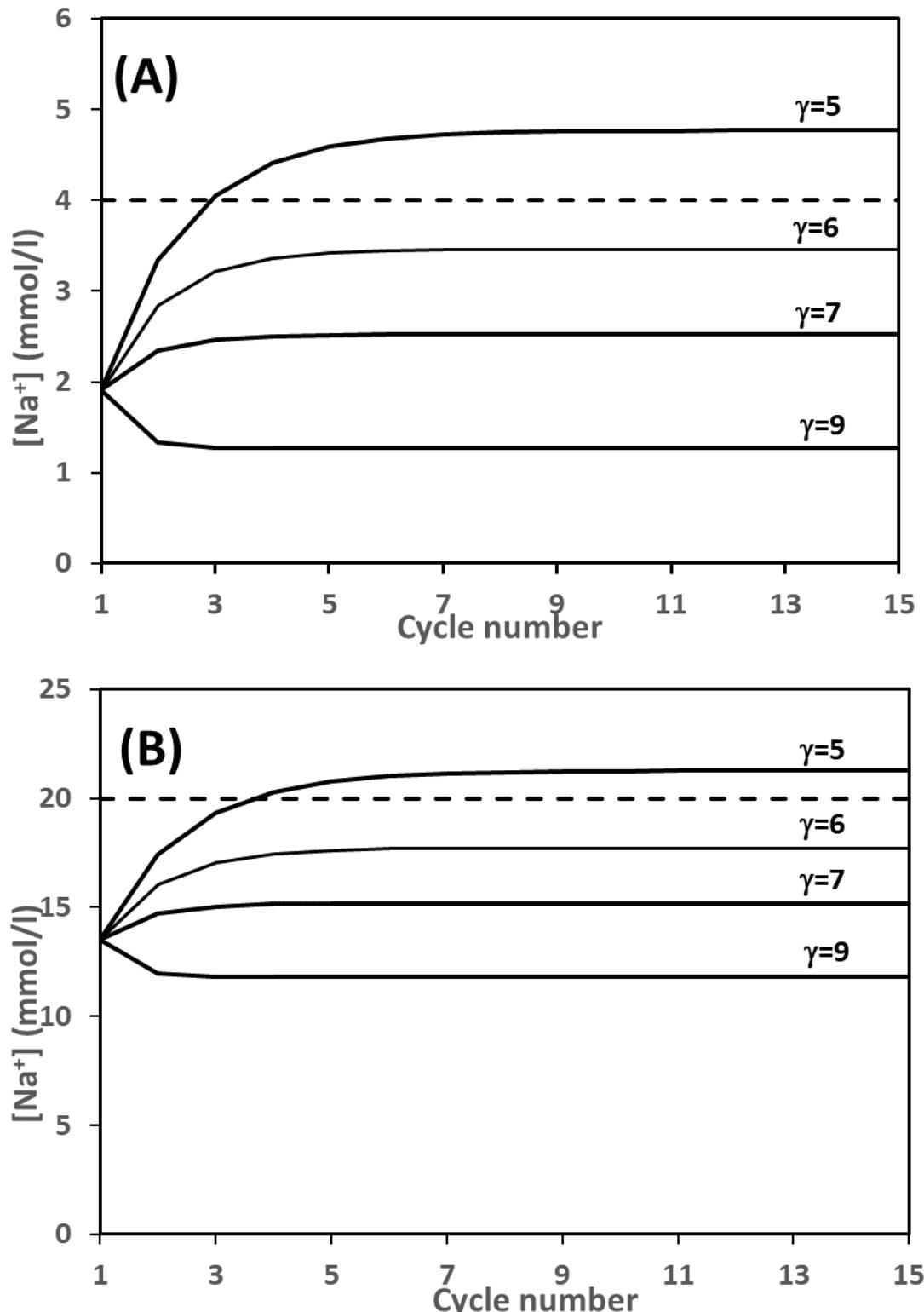
318

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

323

324 Figure 4 explores the relationship between membrane selectivity and the Na⁺ level at
 325 points #0 and #1 during 15 subsequent cycles of operation, given the 10% removal of K⁺
 326 ($\beta = 0.1$) and for a Na⁺ over K⁺ membrane permeability selectivity ranging from 5 to 9. A
 327 membrane selectivity of 5 does not suffice to achieve a steady-state [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, Na⁺ is entering the system from three sources, the
 331 fresh water, the fertilizer content and the Na⁺ leaching from the coconut-based substrate
 332 used. As already remarked, from the second cycle on ε_n adopts a constant numerical
 333 value of $0.25 + 0.44\beta$, i.e., 0.29 for $\beta=0.1$. Given $\theta=0.63$, ξ equals 0.34, implying that the
 334 amount of Na⁺ entering the system from the fresh water and fertilizer is 3 and 72 g/hr,

335 respectively. The 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 Na^+ that needs to be removed by the membrane unit.



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 β of 0.1,
 343 i.e., with 50% - 90% of the Na^+ and 10% of the K^+ removed. Dotted lines represent the
 344 physiological tolerance threshold for tomato of 20 mM (B).
 345

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

363 The volumetric flow Q equals Φ_v(4) = 0.37 × Φ_v(1) = 4.1 × 10⁻⁴ m³/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 α=0.6
366 and β=0.1 (Fig. 4A with γ=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×(3.5+3.1)/0.37=10.7 mM. Note that this concentration difference
369 results in 10.7×10⁻³×23×4000×0.37=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/m² [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⁺, the remaining 40% by
375 K⁺ and other ion species present. Substituting these numbers in Eq. 19 renders a
376 membrane surface area of 70 m². 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 m² 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⁺ content)
385 allows fine tuning of the constant current magnitude applied during operation, and with
386 that the amount of Na⁺ (and K⁺) removed per unit time. Evidently, the implication of
387 such dynamic control is that ϵ_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 μm) and a
396 support porosity of 50% the estimated cost price amounts to 78 euro per m^2 . To put this
397 number in perspective, the price of typical commercially available ion exchange
398 membranes is around 30 euro per 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 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 Na^+ over K^+
415 membrane selectivity. Even though the cost for re-supplementing the IW with 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⁺ 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⁺
432 while preserving the (nutrient) K⁺ as much as possible. Based on real-life process
433 parameters, the present study indicates that a Na⁺ over K⁺ membrane permeation
434 selectivity of 6 already suffices to remain the Na⁺ level the plants are exposed to below
435 20 mM, at least if accepted that 10% of the K⁺ is removed as well. If implemented in an
436 electro dialysis set-up while assuming a constant current density of 10 A/m², the
437 estimated total membrane surface is 70 m². 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

523 **Supporting information**

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

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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 ε and the K^+ and Na^+ concentrations during the
531 1st and 2nd cycle of operation. Here the expressions for the Na^+ concentrations at the
532 three reference points during the 2nd 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)

539 $[Na^+]_{2,2} =$
540 $[(M - X)[\varepsilon_2(1 - \alpha) + \varepsilon_1(1 - \alpha)^2] + (X + L)(1 - \alpha)^2 + (\Theta X + L)(1 - \alpha)]/(1 - \theta)$
541 (3)

542 As shown in the manuscript (Eq. 16), from the 2nd cycle on ε_n becomes constant:

543 $\varepsilon_n = \frac{[K^+]_{0,n}(1 - (1 - \beta)(1 - \mu)) - \theta \times \Psi}{N - \Psi}$ (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 ε_3 is known, $[\text{Na}^+]_{0,3}$ is given by:

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

554 ***Reference point #1***

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

$$[\text{Na}^+]_{1,3} = [(M - X) \times [\varepsilon_3 + \varepsilon_2(1 - \alpha) + \varepsilon_1(1 - \alpha)^2]] + (1 - \alpha)^2(X + L) + (1 - \alpha) \times (X\theta + L) + X\theta + L]/(1 - \theta) \quad (6)$$

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:

$$[\text{Na}^+]_{2,3} = [(M - X) \times [\varepsilon_3(1 - \alpha) + \varepsilon_2(1 - \alpha)^2 + \varepsilon_1(1 - \alpha)^3]] + (1 - \alpha)^3(X + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L)]/(1 - \theta) \quad (7)$$

563

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

565 ***Reference point #0***

$$[\text{Na}^+]_{0,4} = (M - X) \times [\varepsilon_4 + \varepsilon_3(1 - \alpha) + \varepsilon_2(1 - \alpha)^2 + \varepsilon_1(1 - \alpha)^3] + (1 - \alpha)^3(X + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta \quad (8)$$

568 ***Reference point #1***

$$[\text{Na}^+]_{1,4} = [(M - X) \times [\varepsilon_4 + \varepsilon_3(1 - \alpha) + \varepsilon_2(1 - \alpha)^2 + \varepsilon_1(1 - \alpha)^3]] + (1 - \alpha)^3(X + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta + L]/(1 - \theta) \quad (9)$$

571 ***Reference point #2***

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

(10)

574

575

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

577 *Reference point #0*

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

(11)

581

582 *Reference point #1*

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

585 *Reference point #2*

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

588 Generalized expressions for the n^{th} irrigation cycle ($n \geq 2$)

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

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

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⁺ and K⁺ 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⁺ but includes a membrane unit for
15 the selective removal of Na⁺ as well. As determined by the membrane properties, some
16 of the K⁺ is removed as well. Based on real-life process parameters, the model calculates
17 the Na⁺ and K⁺ concentration at three reference points. These process parameters
18 include the evapotranspiration rate, the K⁺ uptake by the plants, the Na⁺ and K⁺ content
19 of the fertilizer, the Na⁺ leaching out from the hydroponic substrate material, and the
20 Na⁺ and K⁺ removal efficiency of the membrane unit. Using these parameters and given a
21 constant K⁺ concentration of the irrigation water entering the greenhouse of 6.6 mM
22 (resulting in the optimal K⁺ 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 Na^+ over K^+
26 selectivity of 6, after a number of cycles the 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; Na^+ over 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. Na^+
40 is a typical example of an ion that over time builds up in the IW [2]. High 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 Na^+ , the IW 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 Na^+ level in the IW during crop growth.
45 Despite the detrimental effects at higher levels, plants do show a certain tolerance for
46 Na^+ . Reported 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 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 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 Na^+ from the IW. A complication arises
53 from the fact that K^+ , an essential plant nutrient, has very similar physicochemical
54 properties as 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 Na^+ and K^+ , respectively.
56 However, a key (physiological) difference between the two ion species is that Na^+ is
57 hardly taken up by the plant and is the major cause of salinity toxicity [11, 12]. Excess
58 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 Na^+ .

61 The fact that Na^+ and 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 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⁺ 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⁺ 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.

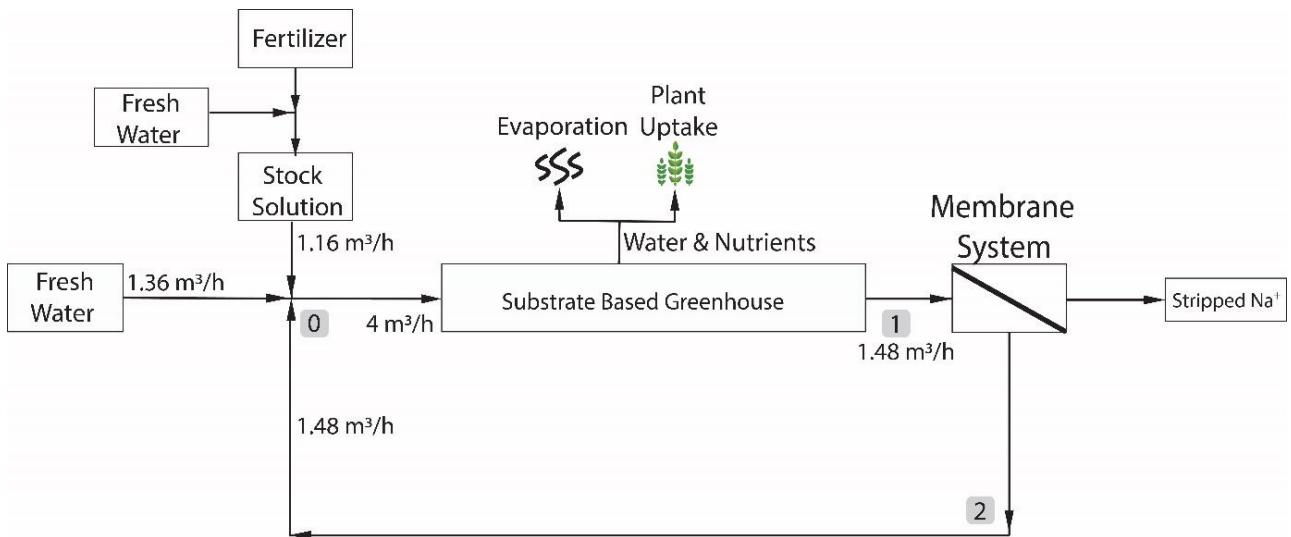
79 The technological challenge thus is to develop a separation membrane that permeates
80 Na⁺ but not, or at least to a much lower extent, K⁺. Obviously, the less permeable for K⁺,
81 the less K⁺ needs to be re-supplied to compensate for this loss. Therefore, a key question
82 for the membrane-to-be-developed concerns its required Na⁺ over K⁺ permeation
83 selectivity. Crucial here to realize is that there is no need to remove all Na⁺. Instead, all
84 that needs to be achieved is a (steady-state) concentration of Na⁺ below the threshold
85 for, in this case, tomato cultivation. Apart from the fact that total Na⁺ 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⁺ re-supply and, even more 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⁺ over K⁺ permeation selectivity and K⁺
91 and Na⁺ permeability and flux, given real-life operational process parameters (e.g., K⁺
92 uptake by tomato, optimal K⁺ level in the IW, evapotranspiration). The simulation study
93 presented here is based on the calculation of the K⁺ and Na⁺ 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^+ 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^+ uptake by the tomato plants and evapotranspiration, the optimal K^+
 128 concentration of the IW entering the greenhouse is 6.6 mM whereas the (detrimental)
 129 threshold Na^+ 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^+ and 2.7 mM Na^+ (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^+ and Na^+ 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⁺ and Na⁺ 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⁺ and Na⁺,
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⁺ concentration*. K⁺ enters the system from two potential sources:

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

148 Furthermore, K⁺ leaves the system at two locations. Firstly, the nutritional K⁺ uptake by
149 the crops and, secondly, the loss through the membrane unit due to the given Na⁺ over
150 K⁺ permeation selectivity of the membrane. Given the optimal K⁺ 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⁺ uptake
153 by the plants (μ) has been determined experimentally by measuring the K⁺
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⁺ entering the
156 greenhouse (6.6 mM):

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

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

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

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

163 Because 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 Na⁺ concentration in the irrigation water
165 is 1.9 mM (resulting from the background Na⁺ concentrations in both fresh water and
166 fertilizer and fixing the K⁺ concentration at point #0 at 6.6 mM). The Na⁺ leaching from
167 the substrate was determined by measuring the 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 Na⁺ is washed out the substrate, the present study
170 assumes a constant degree of leaching during the consecutive cycles of operation.

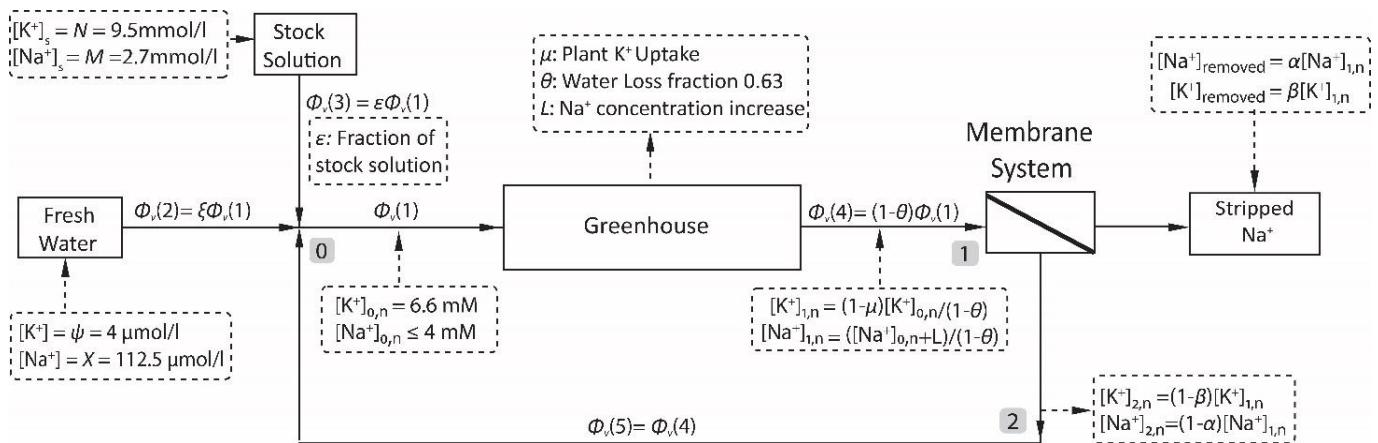
171 The membrane unit needs to remove Na⁺ to meet a (steady-state) Na⁺ concentration
172 level in the irrigation water <20 mM, i.e., the upper tolerance level for Na⁺ of tomato
173 cultivation. Noteworthy, the model assumes that the membrane unit does not remove
174 any water. The reason is that the LSM under development is composed of a hydrophobic
175 support impregnated with a hydrophobic solvent containing the Na⁺ selective carrier 15-
176 crown-5. Prior to entering this organic phase, ions need to be dehydrated with the free
177 energy (ΔG) of dehydration (>0) is compensated for by the ΔG 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⁺
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 (ε)
 189 added at point #0. For that reason, we designated ε the master variable in our
 190 simulations. On the same token, K^+ is the master ionic species, dictating, by means of ε ,
 191 the concentration of the slave ionic species Na^+ at point #0 at the start of each new cycle.
 192 Once ε 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
Ψ	K^+ concentration in fresh water
X	Na^+ concentration in fresh water
N	K^+ concentration in fertilizer stock solution
M	Na^+ concentration in fertilizer stock solution
ξ	fraction of fresh water added at point #0
ε	fraction of fertilizer stock solution added at point #0
μ	fraction of K^+ entering the greenhouse taken up by the crop
L	Na^+ concentration increase due to Na^+ leaching out from the coconut-based substrate
θ	fraction of $\Phi_v(1)$ lost due to evapotranspiration
α	fraction of Na^+ removed from the drain water leaving the greenhouse
β	fraction of K^+ removed from the drain water leaving the greenhouse
γ	Na^+ over K^+ permeation selectivity of the membrane unit

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

209 Volumetric flows (Φ_v) are presented as fraction of the flow entering the greenhouse,
 210 $\Phi_v(1)$ with ε the fraction of the stock solution and ξ 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⁺ concentration for tomato and taken into account K⁺
217 uptake and evapotranspiration, the K⁺ concentration at point #0 is set at 6.6 mM. The
218 Na⁺ threshold of 20 mM is the maximum acceptable Na⁺ level of the IW leaving the
219 greenhouse. Given the Na⁺ leaching out the substrate (3.1 mM) and the
220 evapotranspiration (0.67), the 20 mM translates into a Na⁺ of the IW entering the
221 greenhouse of 20x0.37-3.1=4.3 mM. Throughout this study the threshold Na⁺ 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 Ψ and N are the K⁺ concentration in the fresh water and in the fertilizer stock
226 solution, respectively. Then, according to Eq. 1, the K⁺ 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⁺ 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 Ψ and N being known, the value of ε_1 is defined.

233 Once ε_1 is known, the Na⁺ 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^+ concentration of the stock solution and fresh water,
236 respectively.

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

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

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

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

247

248 **Reference point #2**

249 Reference point #2 is located downstream the membrane unit (permeate side) and
250 calculation of the K^+ and Na^+ concentration at this point therefore requires
251 implementation of the membrane characteristics. Let α be the fraction of Na^+ (compared
252 to reference point #1) that permeates the membrane (and with that removed from the
253 system) and β the fraction of K^+ that permeates the membrane (also removed from the
254 system). Then the K^+ and Na^+ concentrations are given by $[\text{K}^+]_{2,1} = (1 - \theta)[\text{K}^+]_{1,1}$ and
255 $[\text{Na}^+]_{2,1} = (1 - \alpha)[\text{Na}^+]_{1,1}$, 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:

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

266 In analogy with Eq. 2, Eq. 10 results in a K⁺ concentration and ε_2 at point #0 of:

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

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

Once ε_2 has been determined, $[\text{Na}^+]$ at each point can be calculated:

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

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

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

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

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

addition, from the second cycle onwards ε_n remains constant as well and independent of

276 n . This can be seen after, first, substituting ε_1 into $[K^+]_{2,1}$ followed by substituting $[K^+]_{2,1}$
 277 into ε_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, ε_n adopts a numerical value expressed in
 280 terms of β 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 ε and by implication the $[K^+]$ and $[Na^+]$ as
 284 well can all be expressed exclusively in terms of the known process parameters $[K^+]_{0,1}$, α ,
 285 β , μ , θ , r , N , M , X and Ψ . 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 2nd cycle
 293 on are given below (for their derivation, see Supplementary Information).

$$294 \quad [Na^+]_{0,n} = (M - X) \sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i}] + (X\theta + L) \sum_{i=1}^{n-2} [(1 - \alpha)^i] + (X + L)(1 - \alpha)^{(n-1)} + X\theta \\ 295 \quad (17)$$

$$296 \quad [Na^+]_{1,n} = \frac{1}{(1-\theta)} [\sum_{i=1}^n [\varepsilon_i \times (1 - \alpha)^{n-i}] + [(X\theta + L) \sum_{i=1}^{n-1} (1 - \alpha)^{(i-1)}]] + (1 - \alpha)^{(n-1)} \times \\ 297 \quad (X + L)] \quad (18)$$

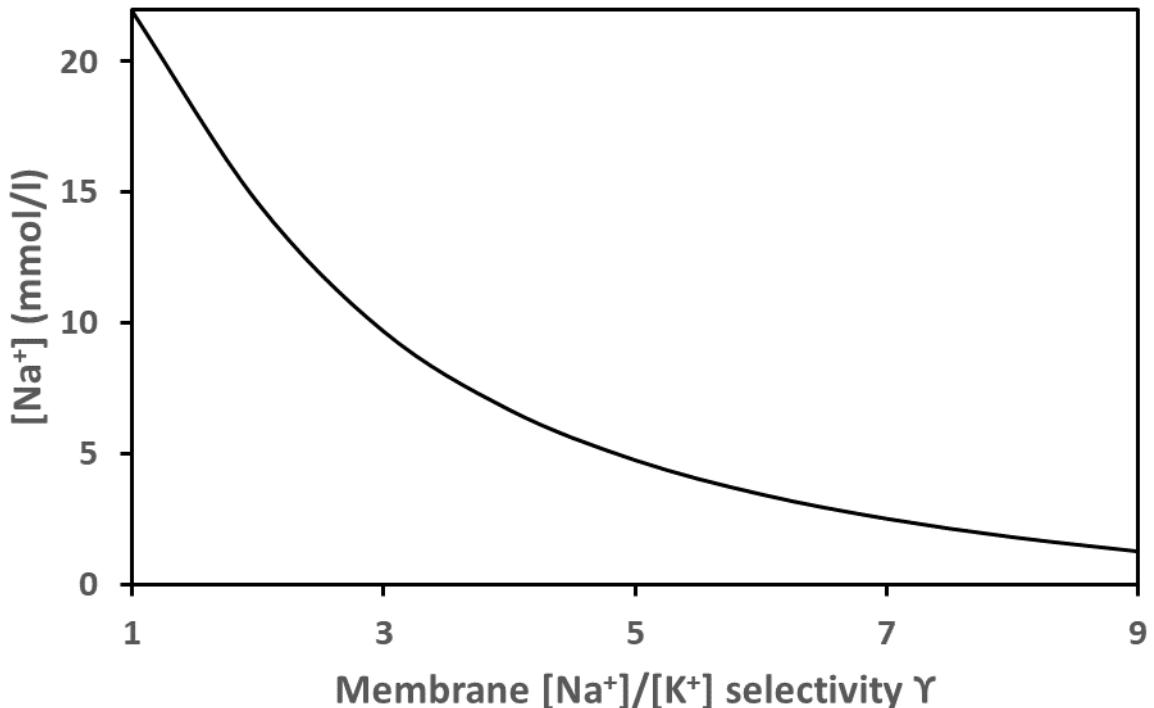
298 Note that for $n=2$ and after a number of repeated substitutions, Eqs. 17 and 18 reduce to
299 Eqs. 13 and 14, respectively.

300 **4. Results and discussion**

301 **4.1 Membrane selectivity**

302 The Na^+ over 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 (γ)
304 required to maintain the Na^+ concentration in the IW below the upper tolerance level of
305 4-5 mM. Because the membrane selectivity (γ) is defined as the ratio of its permeability
306 towards Na^+ (α) and its permeability towards K^+ (β), the permeation of both ion species
307 is coupled. With both β and γ set at a fixed value, α can be calculated and with that the
308 Na^+ level at point #2, which, in turn, allows the calculation of the Na^+ level at point #0 at
309 the start of a new cycle.

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



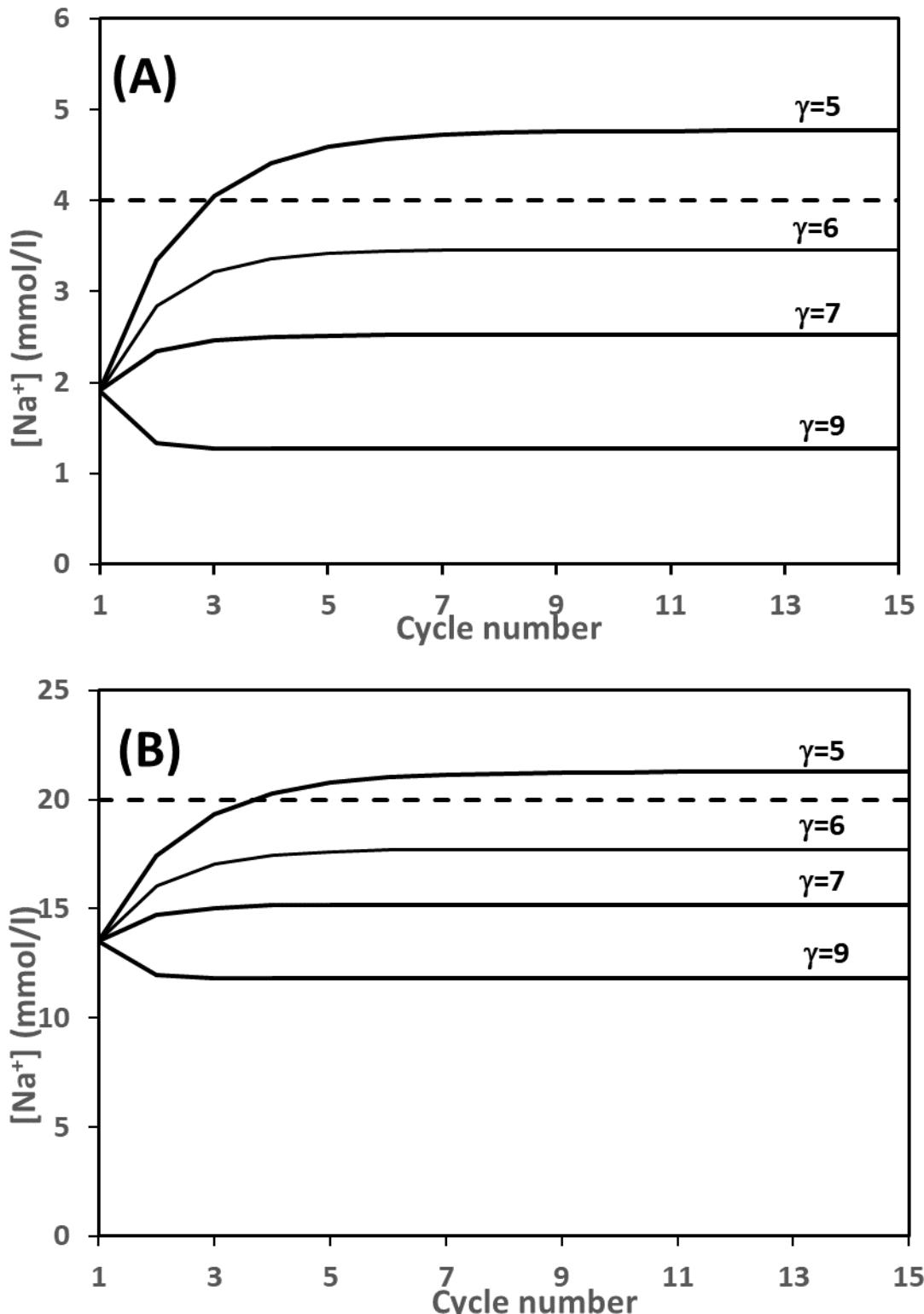
318

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

323

324 Figure 4 explores the relationship between membrane selectivity and the Na⁺ level at
 325 points #0 and #1 during 15 subsequent cycles of operation, given the 10% removal of K⁺
 326 ($\beta = 0.1$) and for a Na⁺ over K⁺ membrane permeability selectivity ranging from 5 to 9. A
 327 membrane selectivity of 5 does not suffice to achieve a steady-state [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, Na⁺ is entering the system from three sources, the
 331 fresh water, the fertilizer content and the Na⁺ leaching from the coconut-based substrate
 332 used. As already remarked, from the second cycle on ε_n adopts a constant numerical
 333 value of $0.25 + 0.44\beta$, i.e., 0.29 for $\beta=0.1$. Given $\theta=0.63$, ξ equals 0.34, implying that the
 334 amount of Na⁺ entering the system from the fresh water and fertilizer is 3 and 72 g/hr,

335 respectively. The 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 Na^+ that needs to be removed by the membrane unit.



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 β 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]:

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

363 The volumetric flow Q equals $\Phi_v(4) = 0.37 \times \Phi_v(1) = 4.1 \times 10^{-4} m^3/s$. 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^2 [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^+ , the remaining 40% by
375 K^+ and other ion species present. Substituting these numbers in Eq. 19 renders a
376 membrane surface area of 70 m^2 . 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^2 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^+ content)
385 allows fine tuning of the constant current magnitude applied during operation, and with
386 that the amount of Na^+ (and K^+) removed per unit time. Evidently, the implication of
387 such dynamic control is that ε_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 μm) and a
396 support porosity of 50% the estimated cost price amounts to 78 euro per m^2 . To put this
397 number in perspective, the price of typical commercially available ion exchange
398 membranes is around 30 euro per 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 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 Na^+ over K^+
415 membrane selectivity. Even though the cost for re-supplementing the IW with 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⁺ 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⁺
432 while preserving the (nutrient) K⁺ as much as possible. Based on real-life process
433 parameters, the present study indicates that a Na⁺ over K⁺ membrane permeation
434 selectivity of 6 already suffices to remain the Na⁺ level the plants are exposed to below
435 20 mM, at least if accepted that 10% of the K⁺ is removed as well. If implemented in an
436 electro dialysis set-up while assuming a constant current density of 10 A/m², the
437 estimated total membrane surface is 70 m². 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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520

521

522 **Supporting information**

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

525 Z. Qian ^{a,c}, H. Miedema ^c, L.C.P.M. de Smet ^{b,c}, E.J.R. Sudhölter ^a

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, $[Na^+]_{2,3}$
528 refers to the Na^+ concentration at point #2 during the third cycle.

529 The manuscript gives the equations for ε and the K^+ and Na^+ concentrations during the
530 1st and 2nd cycle of operation. Here the expressions for the Na^+ concentrations at the
531 three reference points during the 2nd 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 $[Na^+]_{0,2} = (M - X)[\varepsilon_2 + \varepsilon_1(1 - \alpha)] + (X + L)(1 - \alpha) + \Theta X$
535 (1)

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

538 $[Na^+]_{2,2} =$
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 2nd cycle on ε_n becomes constant:

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

543

544 Apart from the fact that $[K^+]_{0,n}$ remains constant for $n > 1$ (6.6 mM), $[K^+]_{1,n}$ and $[K^+]_{2,n}$ 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^+ 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 ε_3 is known, $[\text{Na}^+]_{0,3}$ is given by:

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

553 **Reference point #1**

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

$$[\text{Na}^+]_{1,3} = [(M - X) \times [\varepsilon_3 + \varepsilon_2(1 - \alpha) + \varepsilon_1(1 - \alpha)^2]] + (1 - \alpha)^2(X + L) + (1 - \alpha) \times (X\theta + L) + X\theta + L]/(1 - \theta) \quad (6)$$

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:

$$[\text{Na}^+]_{2,3} = [(M - X) \times [\varepsilon_3(1 - \alpha) + \varepsilon_2(1 - \alpha)^2 + \varepsilon_1(1 - \alpha)^3]] + (1 - \alpha)^3(X + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L)]/(1 - \theta) \quad (7)$$

562

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

564 **Reference point #0**

$$[\text{Na}^+]_{0,4} = (M - X) \times [\varepsilon_4 + \varepsilon_3(1 - \alpha) + \varepsilon_2(1 - \alpha)^2 + \varepsilon_1(1 - \alpha)^3] + (1 - \alpha)^3(X + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta \quad (8)$$

567 **Reference point #1**

$$[\text{Na}^+]_{1,4} = [(M - X) \times [\varepsilon_4 + \varepsilon_3(1 - \alpha) + \varepsilon_2(1 - \alpha)^2 + \varepsilon_1(1 - \alpha)^3]] + (1 - \alpha)^3(X + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta + L]/(1 - \theta) \quad (9)$$

570 **Reference point #2**

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

573

574

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

576 ***Reference point #0***

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

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

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

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 nth 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 $[Na^+]_{0,n}$ as function of n :

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

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

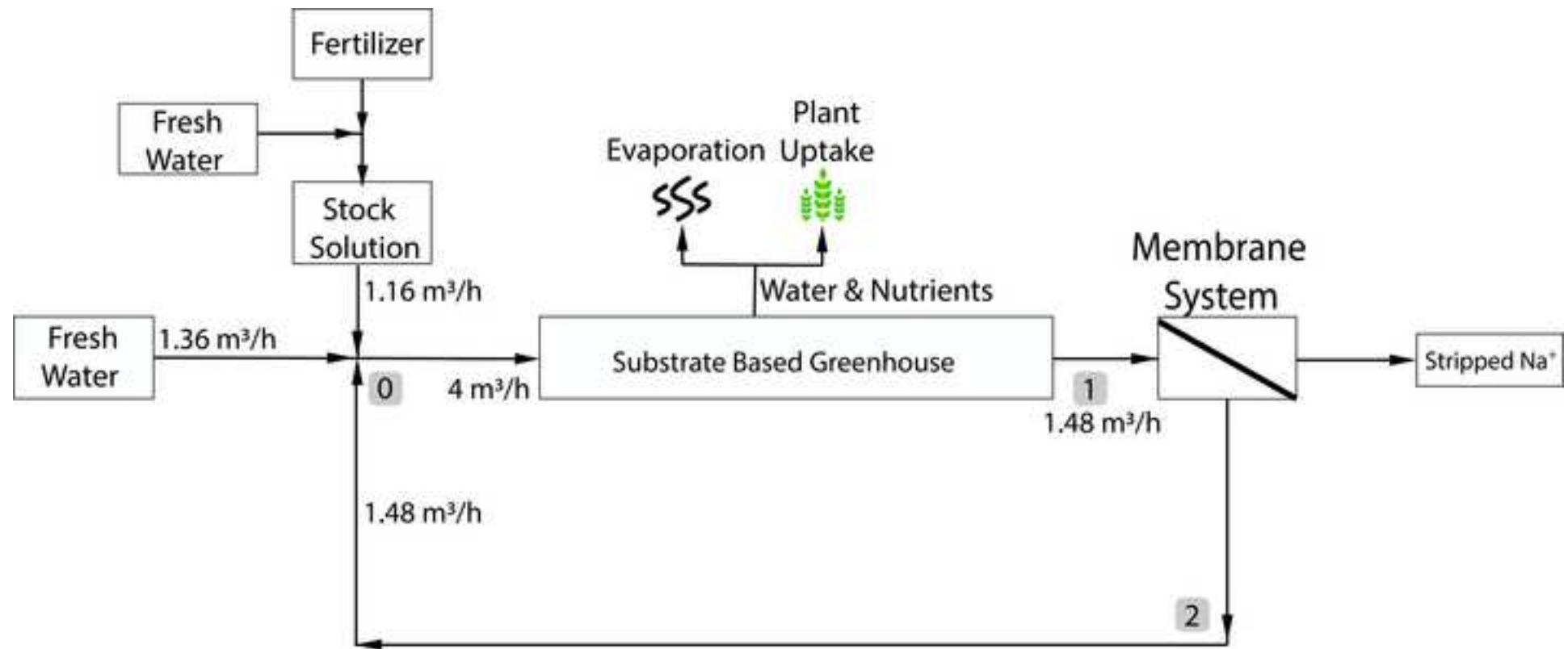


Figure 2

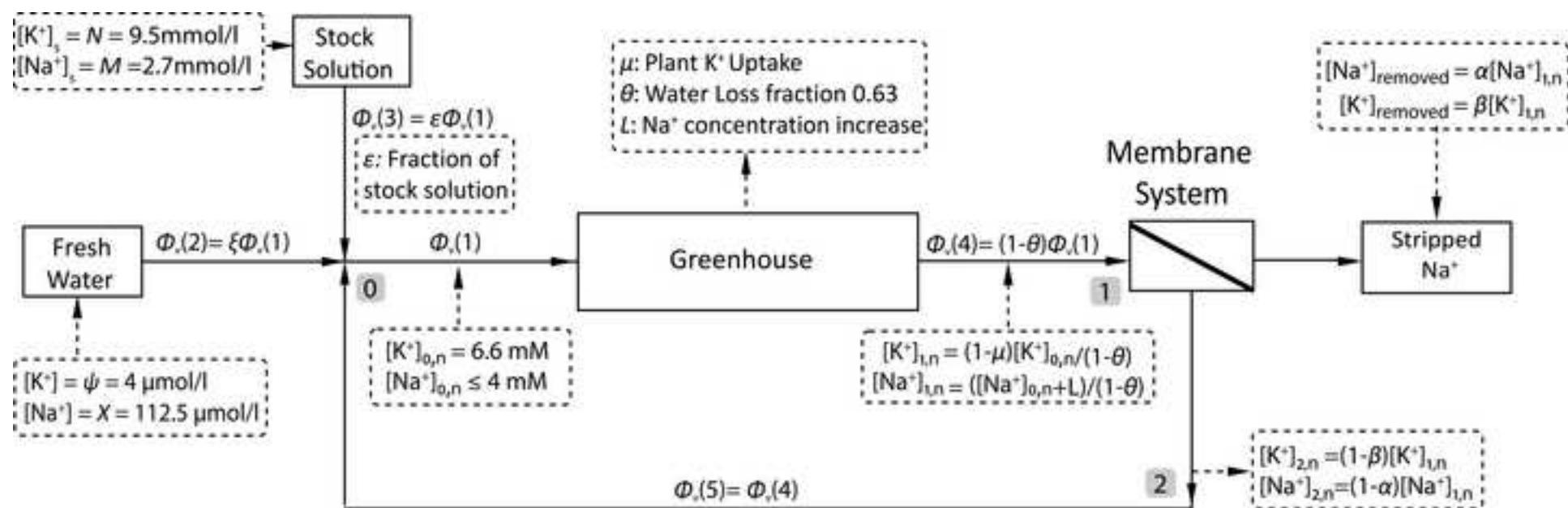


Figure 3

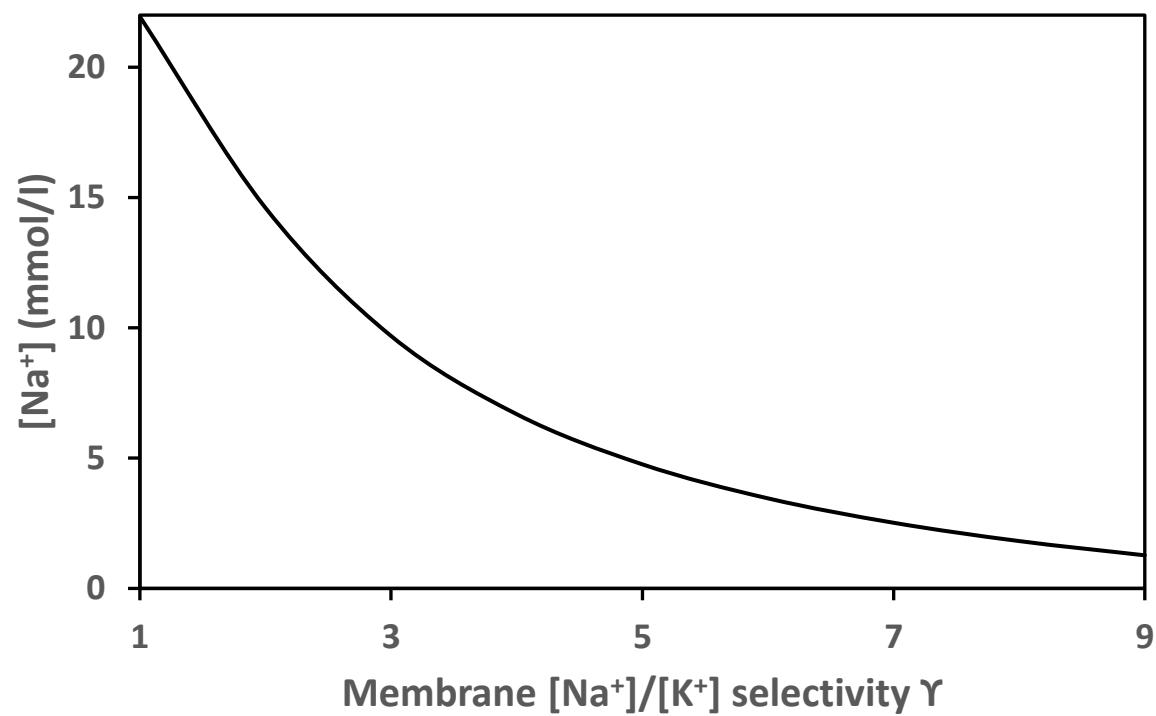
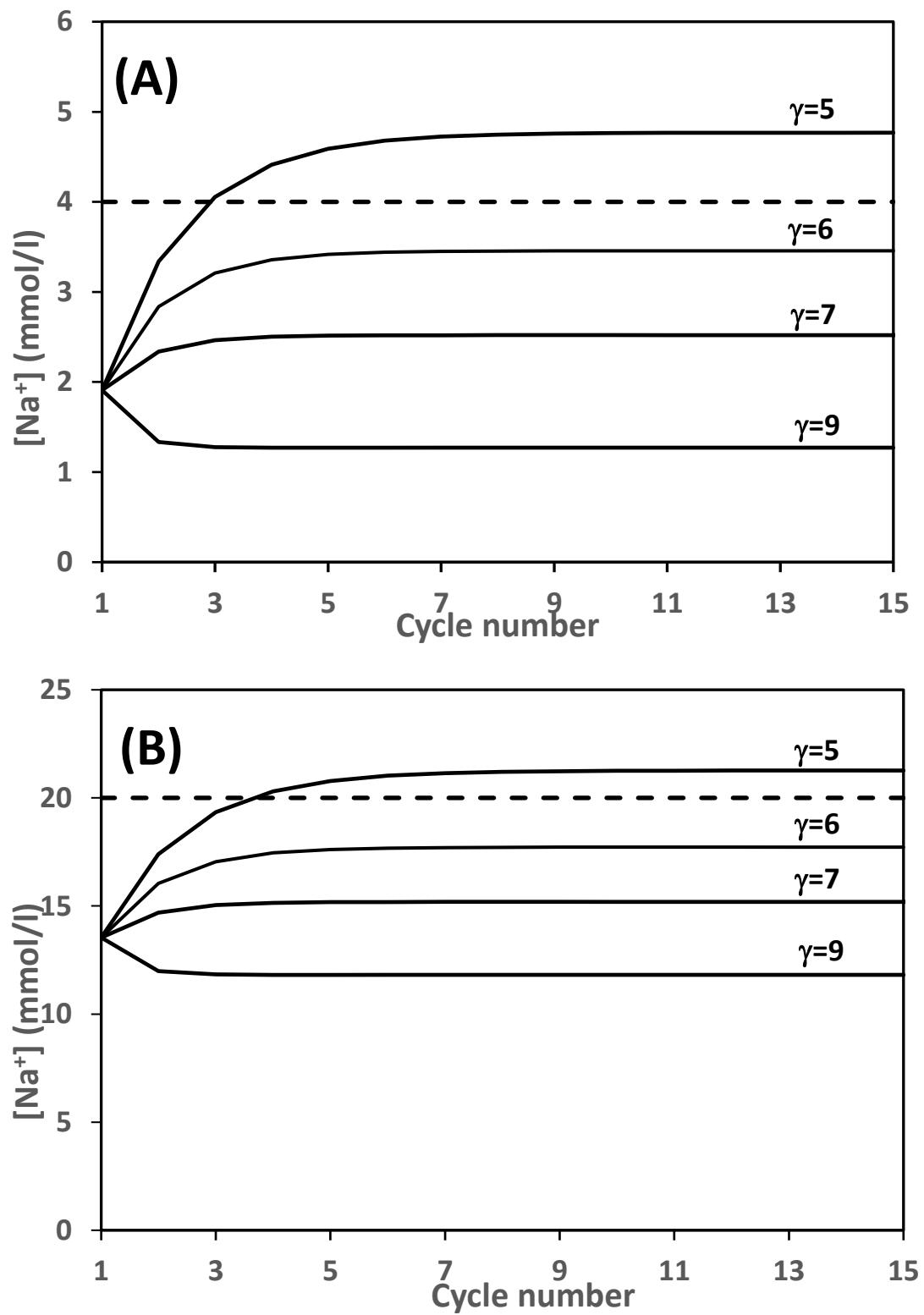


Figure 4



Variables	Values
$\Phi_v(1)$	Volumetric flow entering the greenhouse 4 m ³ /hr
Ψ	K ⁺ concentration in fresh water 4 μM
X	Na ⁺ concentration in fresh water 112.5 μM
N	K ⁺ concentration in fertilizer stock solution 9.5 mM
M	Na ⁺ concentration in fertilizer stock solution 2.7 mM
ξ	fraction of fresh water added at point #0
ε	fraction of fertilizer stock solution added at point #0
μ	fraction of K ⁺ entering the greenhouse taken up by the crop 0.36
L	Na ⁺ concentration increase due to Na ⁺ leaching out from the coconut-based substrate 3.1 mM
θ	fraction of $\Phi_v(1)$ lost due to evapotranspiration 0.63
α	fraction of Na ⁺ removed from the drain water leaving the greenhouse 0-1
β	fraction of K ⁺ removed from the drain water leaving the greenhouse 0-1
γ	Na ⁺ over K ⁺ permeation selectivity of the membrane unit α/β

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