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.

l5. 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 subsidiues 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.
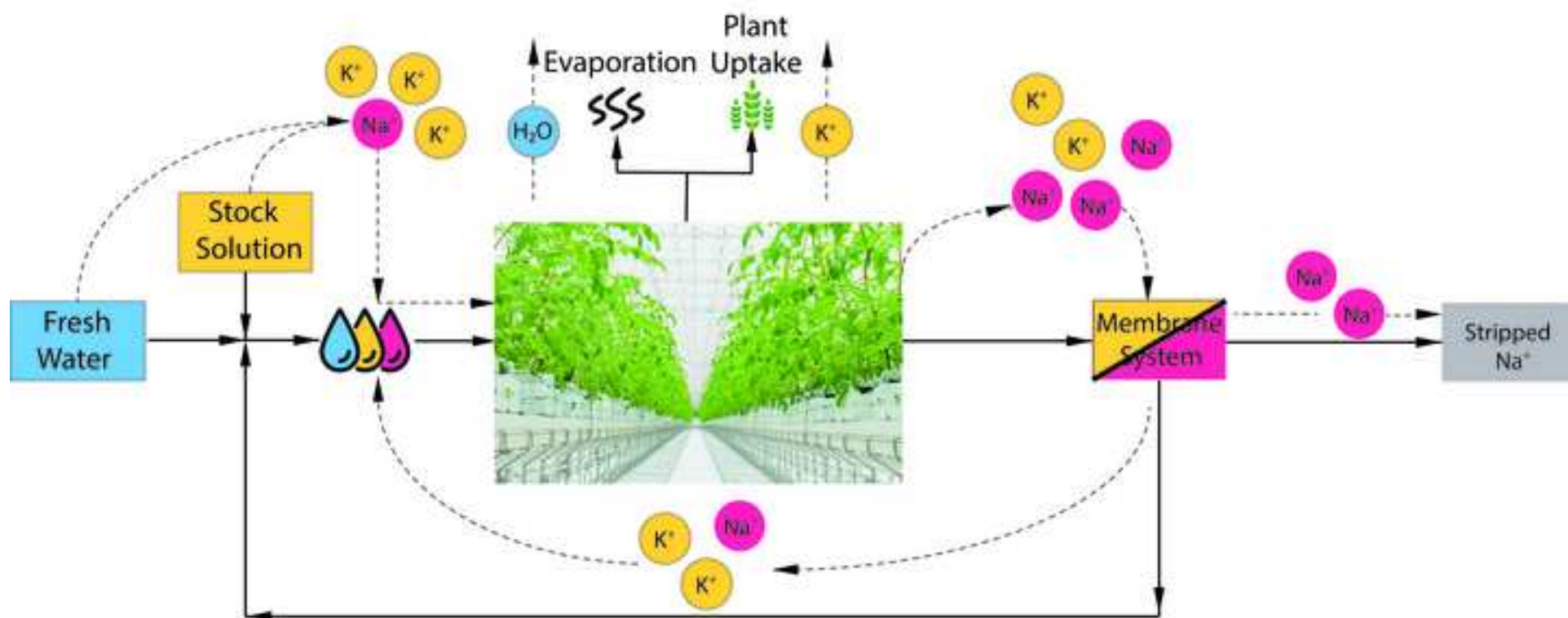
Research Highlights

- 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 m^2.

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

currently is developed in our lab. It is found that even for a limited Na^+ over K^+

selectivity of 6, after a number of cycles the Na^+ level reaches steady state at a level

below the upper (toxic) threshold for tomato cultivation (20 mM). Economic aspects and

ways of implementation of such a system are briefly discussed.

Keywords

Greenhouse; Irrigation water; Sodium removal; Mass balance; Modelling; Na^+ over K^+

membrane selectivity

1. Introduction

Closed-loop soilless or hydroponic systems are already widely used if not, at least in

certain countries e.g. The Netherlands, common practice in horticulture[1]. Nutrients

and water are supplied continuously to the irrigation water (IW) to compensate for

nutrient uptake by the plants and water loss due to evapotranspiration. Ideally, the

nutrient and water supply are fine-tuned such that the nutrient concentration and the

osmotic pressure of the drainage solution remain (fairly) constant. Consequently,

nutrients, which are present but are not taken up by the plant, accumulate in the IW. Na^+

is a typical example of an ion that over time builds up in the IW [2]. High Na^+ levels

inhibit plant growth directly or indirectly by hampering the uptake of other nutrients [3-

6]. Because of the detrimental effects of high Na^+, the IW Na^+ level has been subject of

numerous studies already [7-9]. These studies are restricted however to simulation

studies, validated or not by monitoring the actual Na^+ level in the IW during crop growth.

Despite the detrimental effects at higher levels, plants do show a certain tolerance for

Na^+. Reported Na^+ threshold values for tomato vary somewhat but levels above 5 dS/m,

equivalent to 50 mM, prove to inhibit growth and yield [10]. The threshold value might

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, evenly important, the

89   more sustainable the overall technology. Prime aim of the present study is to explore the

90   required membrane specifications in terms of Na^+ 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

4

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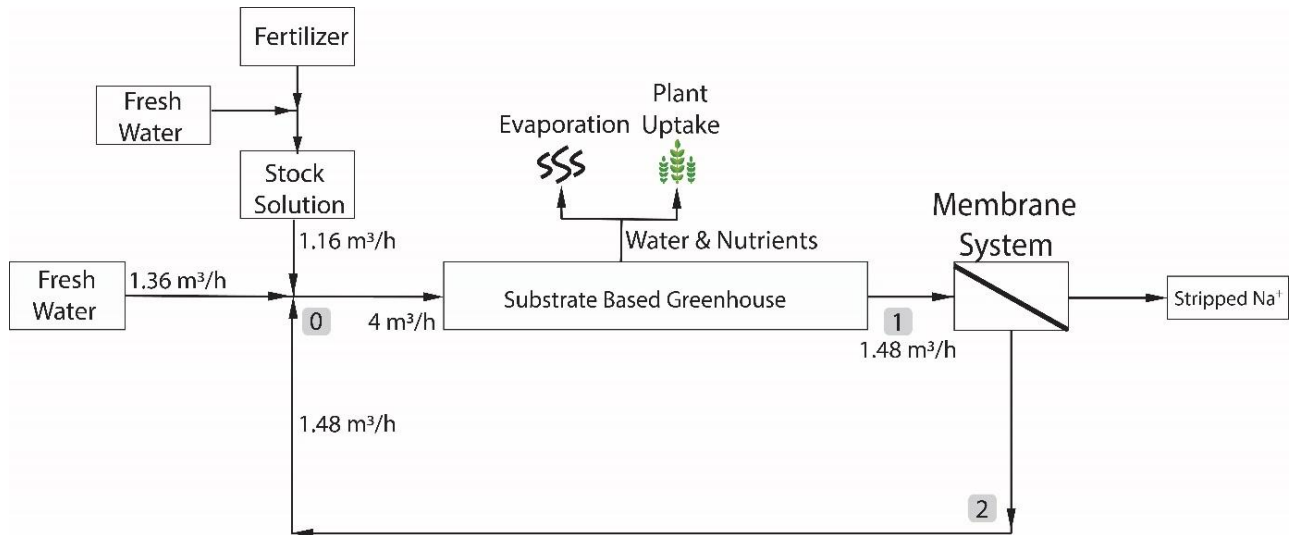
Figure 1. Outline of a substrate-based greenhouse irrigation water system with the drain water recycled and including a membrane unit for the selective removal of Na+. Reference points #0-2 are indicated as well as the relevant (steady-state) volumetric flows while assuming a K+ loss of 10% (i.e., β=0.1).

2.2 Process parameters

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

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

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

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),

7

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

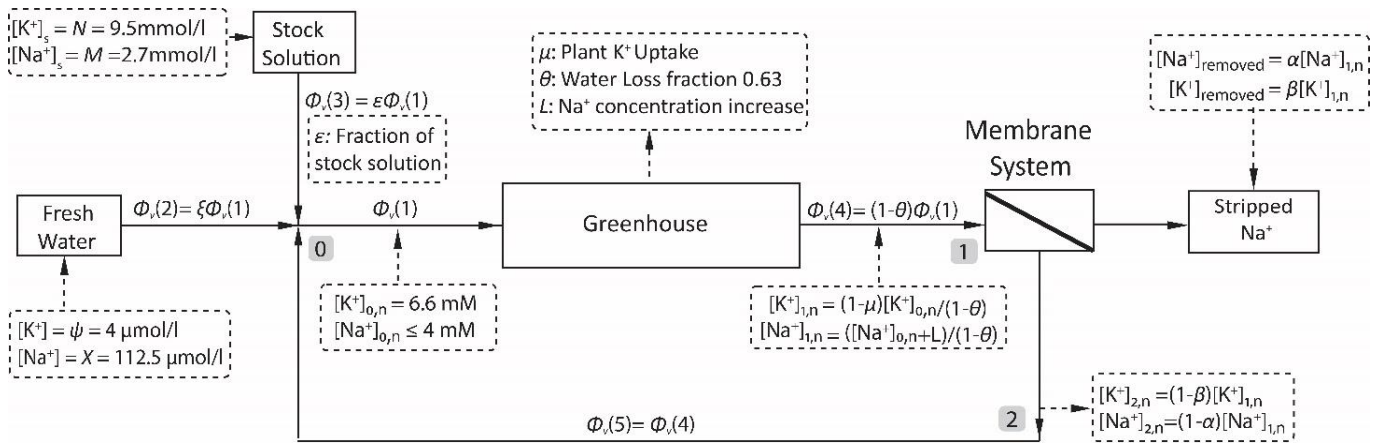170   assumes a constant degree of leaching during the consecutive cycles of operation.

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

8

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.

2.3.1 Volumetric flow balance for the first two cycles

2.3.1.1 First irrigation cycle (n=1)

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

Variables		Values
$\Phi_v(1)$	Volumetric flow entering the greenhouse	4 m³/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.

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

Reference point #0

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

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

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

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

230   The fraction of stock solution thus is:

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

232   With $[K^+]_{0,1} = 6.6\ mM$ 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    $$[Na^+]_{0,1} = \xi_1 X + \varepsilon_1 M = \varepsilon_1(M - X) + X \qquad (5)$$

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 $[K^+]_{0,n}$ is fixed

239 at 6.6 mM, $[K^+]_{1,n}$ is directly proportional to $[K^+]_{0,n}$. Let μ be the fraction of K^+ taken up by

240 the plants and θ the fraction of water loss due to evapotranspiration. Then, $[K^+]_{1,1}$ is

241 given by:

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

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 $[Na+]_{1,1}$ is given by:

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

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 $[K^+]_{2,1}=(1-\beta)[K^+]_{1,1}$ and

255 $[Na^+]_{2,1}=(1-\alpha)[Na^+]_{1,1}$, 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 $\Phi_v(1) = \Phi_v(2) + \Phi_v(3) + \Phi_v(5)$ $\hfill$ (8)

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

263 $\Phi_v(1) = \xi_2\Phi_v(1) + \varepsilon_2\Phi_v(1) + (1 - \Theta)\Phi_v(1)$ $\hfill$ (9)

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

265 $\phi(v, 1) = (\Theta - \varepsilon_2)\phi(v, 1) + \varepsilon_2\phi(v, 1) + (1 - \Theta)(v, 1)$ $\hfill$ (10)

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

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

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

269   Once ε_2 has been determined, $[Na^+]$ at each point can be calculated:

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

271 $[Na^+]_{1,2} = \dfrac{[\varepsilon_2(M-X)+\Theta X]+L}{1-\Theta} + [Na^+]_{2,1}$ $\hfill$ (14)

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

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

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

275   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    $$\varepsilon_n = \frac{[K^+]_{0,n}\left(1-(1-\beta)(1-\mu)\right)-\theta \times \Psi}{N-\Psi}$$ (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 β=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 nth 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    $$[Na^+]_{0,n} = (M-X)\sum_{i=1}^{n}[\varepsilon_i \times (1-\alpha)^{n-i}] + (X\theta + L)\sum_{i=1}^{n-2}[(1-\alpha)^i] + (X+L)(1-\alpha)^{(n-1)} + X\theta$$

295   (17)

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

297   (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
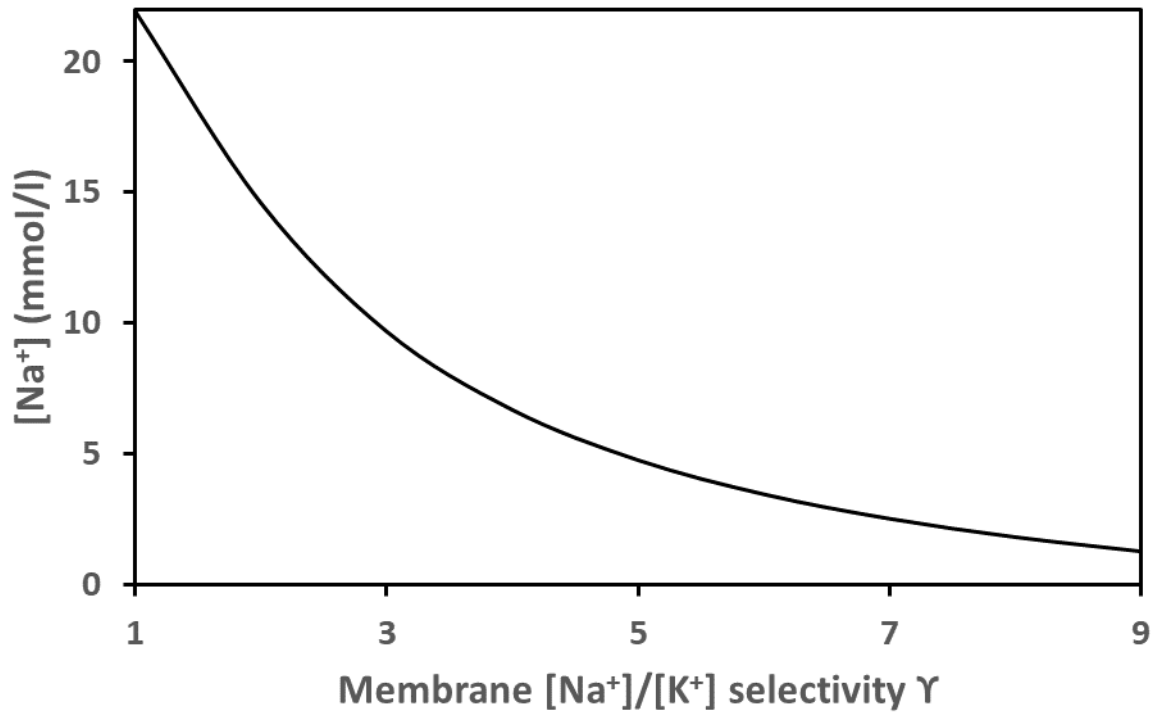
317   after 10 cycles of operation.

318

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

Figure 4 explores the relationship between membrane selectivity and the Na$^+$ level at points #0 and #1 during 15 subsequent cycles of operation, given the 10% removal of K$^+$ (β = 0.1) and for a Na$^+$ over K$^+$ membrane permeability selectivity ranging from 5 to 9. A membrane selectivity of 5 does not suffice to achieve a steady-state [Na$^+$] below the threshold of 4 mM at point #0 (A) and of 20 mM at point #1 (B) . Indeed, it requires at least a selectivity of 6 to accomplish steady-state levels remaining below these thresholds. As indicated in Fig. 2, Na$^+$ is entering the system from three sources, the fresh water, the fertilizer content and the Na$^+$ leaching from the coconut-based substrate used. As already remarked, from the second cycle on ε_n adopts a constant numerical value of $0.25 + 0.44\beta$, i.e., 0.29 for β=0.1. Given θ=0.63, ξ equals 0.34, implying that the amount of Na$^+$ entering the system from the fresh water and fertilizer is 3 and 72 g/hr,

16

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

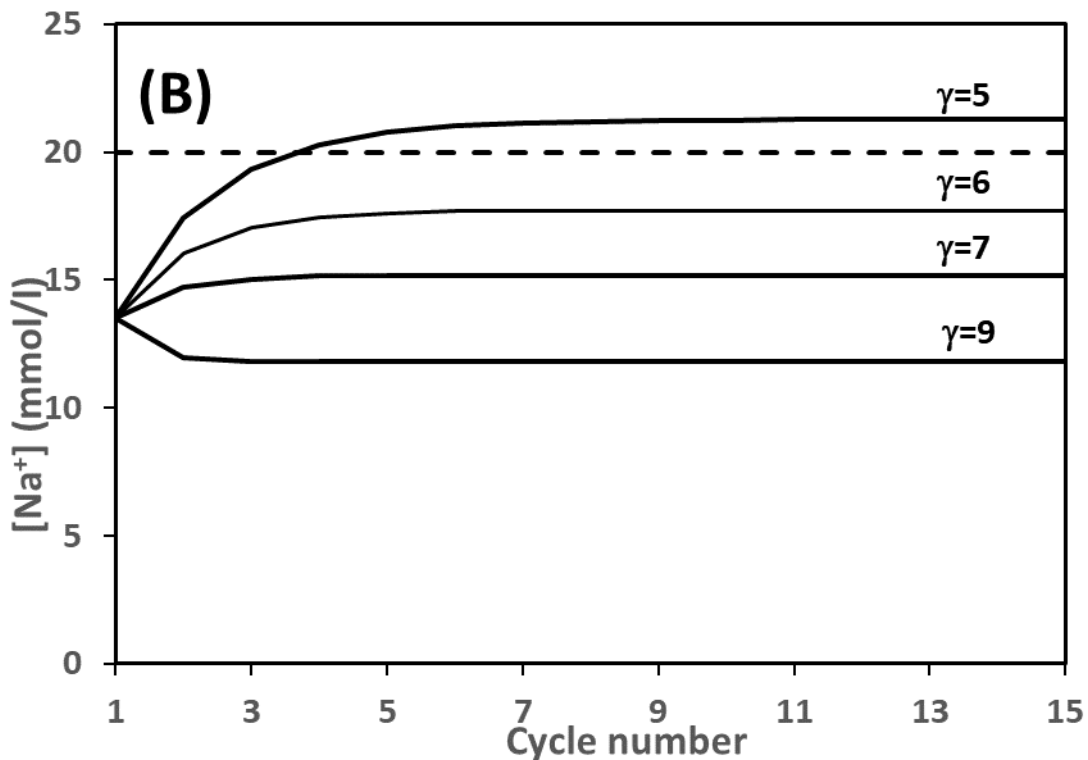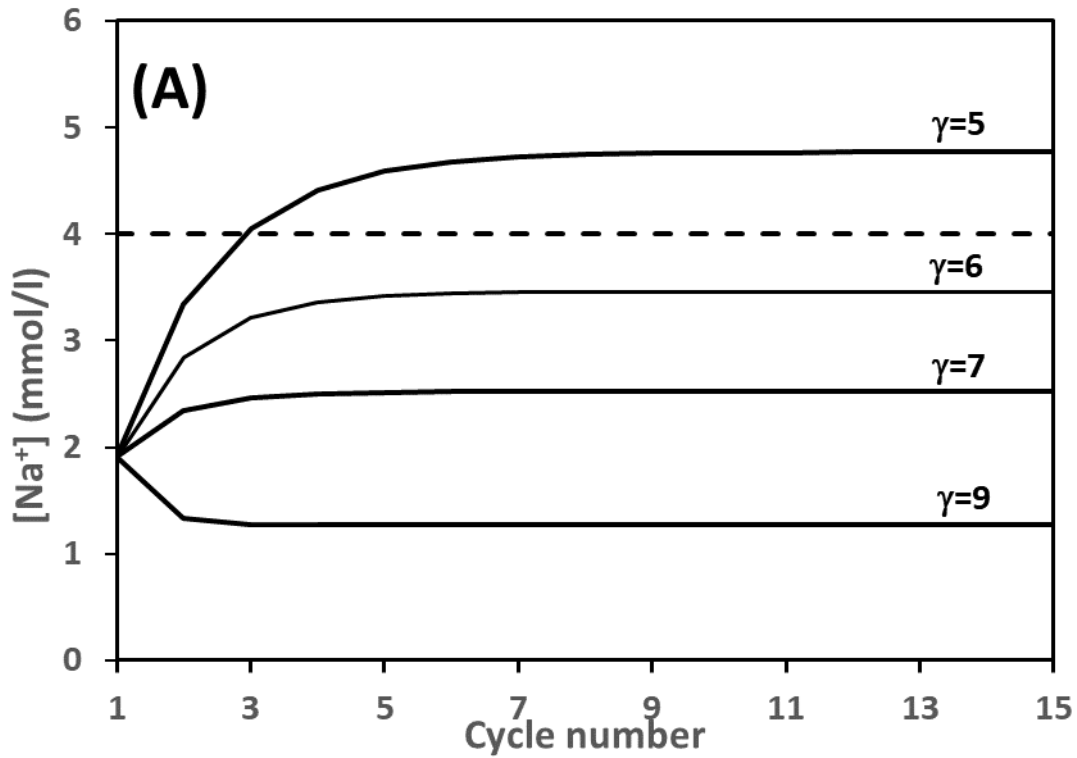337 Na^+ that needs to be removed by the membrane unit.

338

339

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

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

437 estimated total membrane surface is 70 m^2. 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

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

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

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

(1)

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

(2)

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

(3)

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

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

(4)

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

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

550 *Reference point #0*

551 In analogy with Eq. 13 in the manuscript, once ε_3 is known, $[Na^+]_{0,3}$ is given by:

552 $$[Na^+]_{0,3} = \varepsilon_3(M - X) + \varepsilon_2(M - X)(1 - \alpha) + \varepsilon_1(M - X)(1 - \alpha)^2 + (X + L)(1 - \alpha)^2 + (X\theta + L)(1 - \alpha) + X\theta$$

553 (5)

554 *Reference point #1*

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

556 $$[Na^+]_{1,3} = [(M - X) \times [\varepsilon_3 + \varepsilon_2(1 - \alpha) + \varepsilon_1(1 - \alpha)^2)] + (1 - \alpha)^2(X + L) + (1 - \alpha) \times (X\theta + L) + X\theta + L]/(1 - \theta)$$

557 (6)

558

559 *Reference point #2*

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

561 $$[Na^+]_{2,3} = [(M - X) \times [\varepsilon_3(1 - \alpha) + \varepsilon_2(1 - \alpha)^2 + \varepsilon_1(1 - \alpha)^3)] + (1 - \alpha)^3(X + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L)]/(1 - \theta)$$

562 (7)

563

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

565 *Reference point #0*

566 $$[Na^+]_{0,4} = (M - X) \times [\varepsilon_4 + \varepsilon_3(1 - \alpha) + \varepsilon_2(1 - \alpha)^2 + \varepsilon_1(1 - \alpha)^3)] + (1 - \alpha)^3(X + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta$$

567 (8)

568 *Reference point #1*

569 $$[Na^+]_{1,4} = [(M - X) \times [\varepsilon_4 + \varepsilon_3(1 - \alpha) + \varepsilon_2(1 - \alpha)^2 + \varepsilon_1(1 - \alpha)^3)] + (1 - \alpha)^3(X + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta + L]/(1 - \theta)$$

570 (9)

571 *Reference point #2*

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

573 $\qquad$ (10)

574

575

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

577 *Reference point #0*

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

579 $(1 - \alpha)^4(X + L) + (1 - \alpha)^3(X\theta + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta$

580 $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (11)

581

582 *Reference point #1*

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

584 $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (12)

585 *Reference point #2*

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

587 $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (13)

588 ## Generalized expressions for the nth irrigation cycle (n≥2)

589 When comparing Eqs. 1, 5, 8 and 11, the resemblance in the form of the expressions

590 becomes evident. This resemblance allows the formulation of a generalized expression

591 for $[\text{Na}^+]_{0,n}$ as function of *n*:

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

593 $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (14)

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

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

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

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

598    $$(15)$$

599

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

601

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

603    $$(16)$$

604

605

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

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Abstract

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

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

Keywords

1. Introduction

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

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

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

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, evenly important, the

89 more sustainable the overall technology. Prime aim of the present study is to explore the

90 required membrane specifications in terms of Na^+ 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.
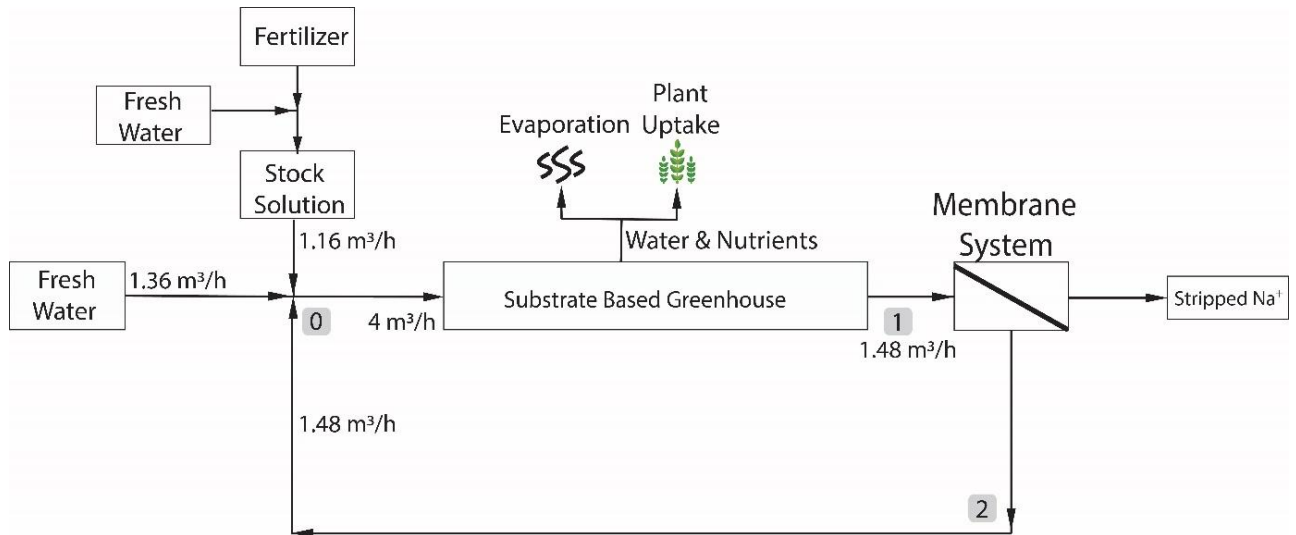
117

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

2.2 Process parameters

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

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

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

6

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):

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

157

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

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

7

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

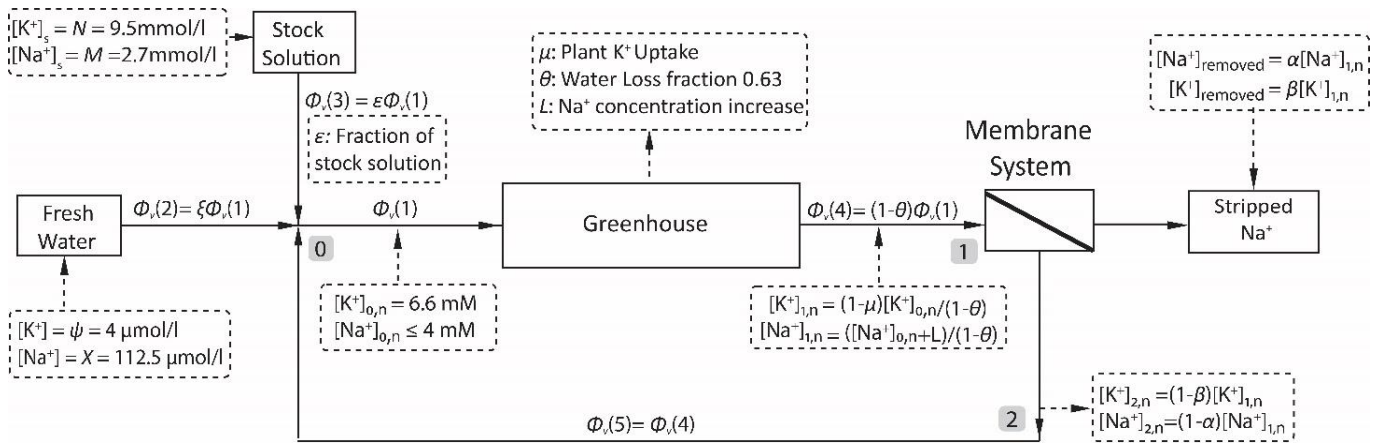170   assumes a constant degree of leaching during the consecutive cycles of operation.

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

8

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.

9

2.3.1 Volumetric flow balance for the first two cycles

2.3.1.1 First irrigation cycle (n=1)

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

Variables		Values
$\Phi_v(1)$	Volumetric flow entering the greenhouse	4 m³/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.

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

Reference point #0

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

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

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

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

230   The fraction of stock solution thus is:

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

232   With $[K^+]_{0,1} = 6.6 \, mM$ 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     $$[Na^+]_{0,1} = \xi_1 X + \varepsilon_1 M = \varepsilon_1(M - X) + X \qquad (5)$$

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 $[K^+]_{0,n}$ is fixed

239 at 6.6 mM, $[K^+]_{1,n}$ is directly proportional to $[K^+]_{0,n}$. Let μ be the fraction of K$^+$ taken up by

240 the plants and θ the fraction of water loss due to evapotranspiration. Then, $[K^+]_{1,1}$ is

241 given by:

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

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 $[Na+]_{1,1}$ is given by:

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

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 $[K^+]_{2,1}=(1-\beta)[K^+]_{1,1}$ and

255 $[Na^+]_{2,1}=(1-\alpha)[Na^+]_{1,1}$, respectively.

256

2.3.1.2 Second irrigation cycle (n=2)

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

$$\Phi_v(1) = \Phi_v(2) + \Phi_v(3) + \Phi_v(5) \tag{8}$$

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

$$\Phi_v(1) = \xi_2\Phi_v(1) + \varepsilon_2\Phi_v(1) + (1 - \Theta)\Phi_v(1) \tag{9}$$

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

$$\phi(v,1) = (\Theta - \varepsilon_2)\phi(v,1) + \varepsilon_2\phi(v,1) + (1 - \Theta)(v,1) \tag{10}$$

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

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

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

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

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

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

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

==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 β=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

13

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 $$\varepsilon_n = \frac{[K^+]_{0,n}(1-(1-\beta)(1-\mu))-\theta \times \Psi}{N-\Psi}$$ (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 β=0.1).

281

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

295 (17)

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

297 (18)

298 <mark>Note that for *n*=2 and after a number of repeated substitutions, Eqs. 17 and 18 reduce to</mark>

299 <mark>Eqs. 13 and 14, respectively.</mark>

4. Results and discussion

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
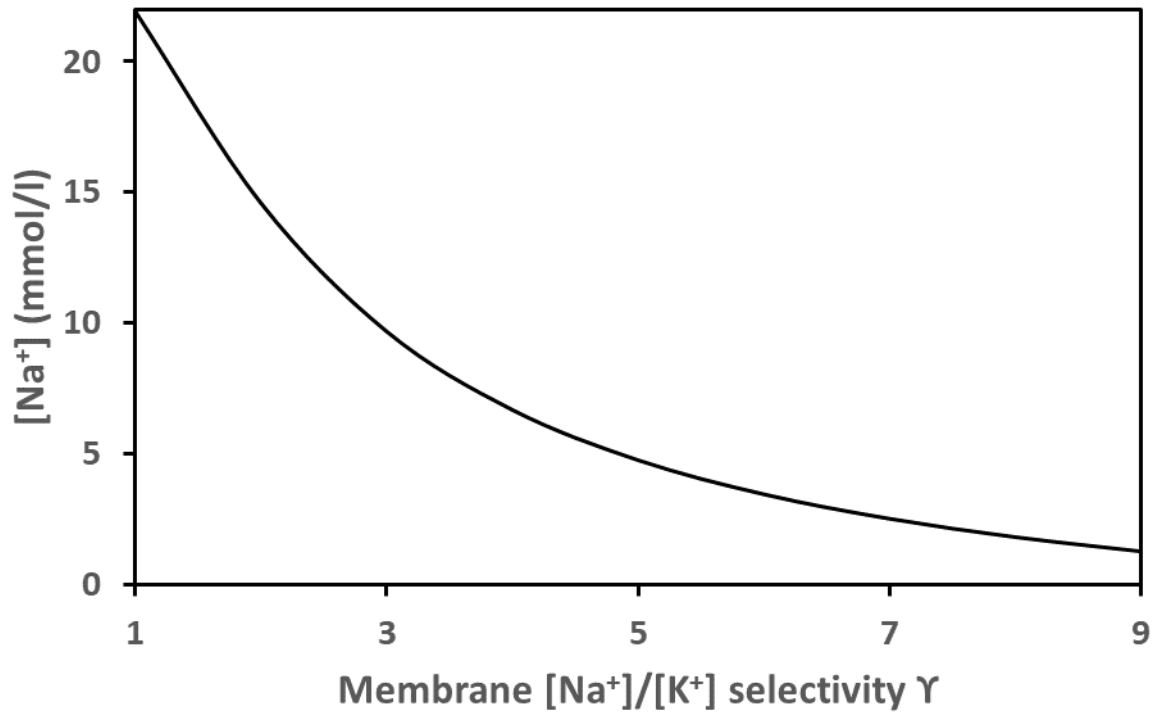
317 after 10 cycles of operation.

318

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

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

16

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

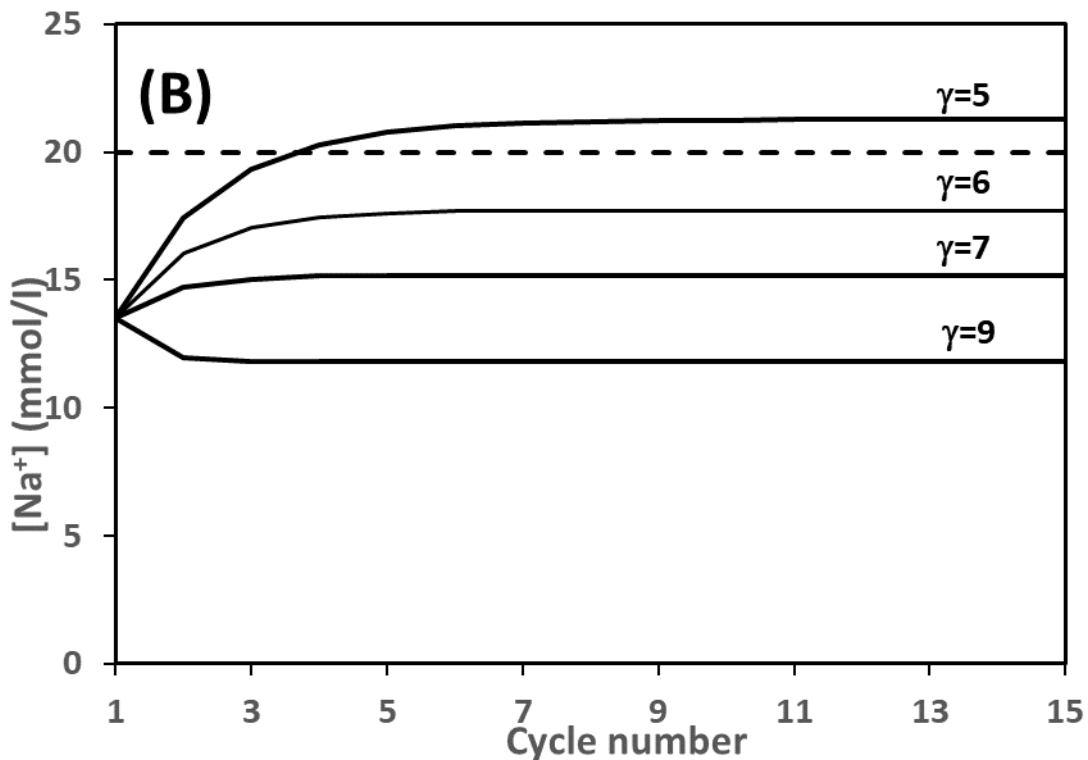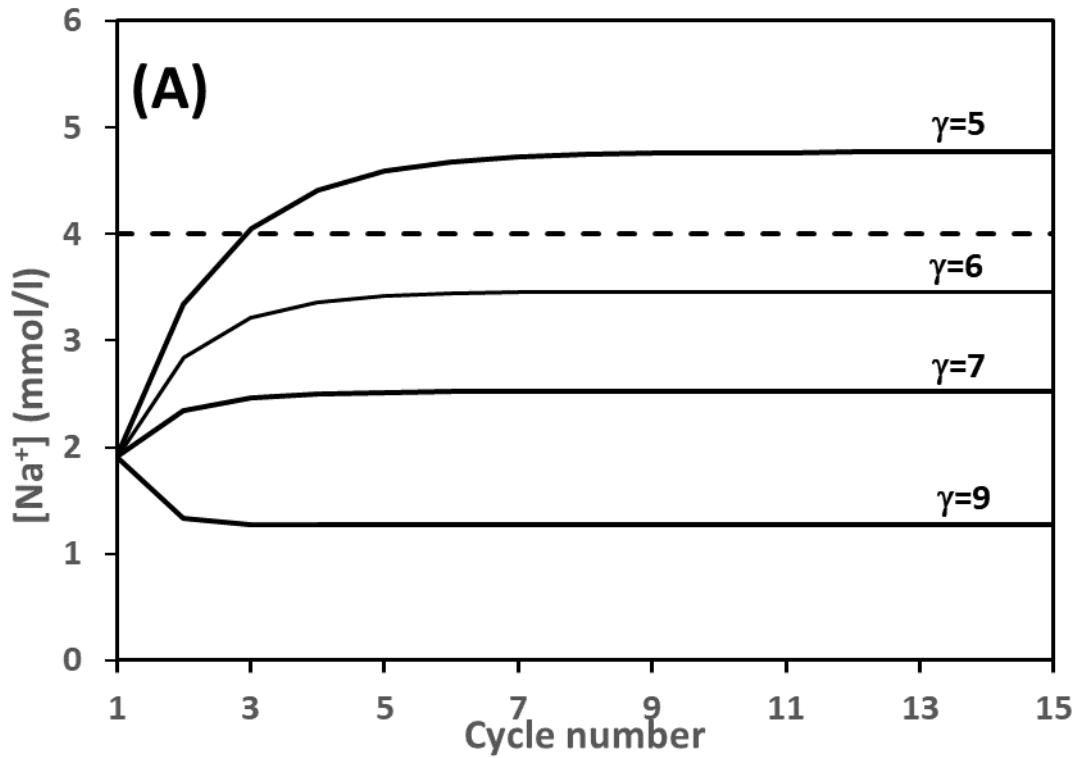337 Na$^+$ that needs to be removed by the membrane unit.

338

339

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

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

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

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 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

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

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

4.3 Economics perspective

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

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

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

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

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/m^2, the

437 estimated total membrane surface is 70 m^2. 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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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)

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

540 (3)

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

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

25

550 In analogy with Eq. 13 in the manuscript, once ε_3 is known, $[Na^+]_{0,3}$ is given by:

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

551
552 $$(5)$$

553 *Reference point #1*

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

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

555
556 $$(6)$$

557

558 *Reference point #2*

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

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

560
561 $$(7)$$

562

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

564 *Reference point #0*

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

565
566 $$(8)$$

567 *Reference point #1*

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

568
569 $$(9)$$

570 *Reference point #2*

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

571
572 $$(10)$$

573

574

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

Reference point #0

$$[\text{Na}^+]_{0.5} = (M - X) \times [\varepsilon_5 + \varepsilon_4(1 - \alpha) + \varepsilon_3(1 - \alpha)^2 + \varepsilon_2(1 - \alpha)^3 + \varepsilon_1(1 - \alpha)^4)] +$$
$$(1 - \alpha)^4(X + L) + (1 - \alpha)^3(X\theta + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta$$

$$(11)$$

Reference point #1

$$[\text{Na}^+]_{1.5} = [(M - X) \times [\varepsilon_5 + \varepsilon_4(1 - \alpha) + \varepsilon_3(1 - \alpha)^2 + \varepsilon_2(1 - \alpha)^3 + \varepsilon_1(1 - \alpha)^4)] +$$
$$(1 - \alpha)^4(X + L) + (1 - \alpha)^3(X\theta + L) + (1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L) + X\theta +$$
$$L]/(1 - \theta)$$

$$(12)$$

Reference point #2

$$[\text{Na}^+]_{2.5} = [(M - X) \times [\varepsilon_5(1 - \alpha) + \varepsilon_4(1 - \alpha)^2 + \varepsilon_3(1 - \alpha)^3 + \varepsilon_2(1 - \alpha)^4 +$$
$$\varepsilon_1(1 - \alpha)^5)] + (1 - \alpha)^5(X + L) + (1 - \alpha)^4(X\theta + L) + (1 - \alpha)^3(X\theta + L) +$$
$$(1 - \alpha)^2(X\theta + L) + (1 - \alpha)(X\theta + L)]/(1 - \theta)$$
$$(13)$$

Generalized expressions for the nth irrigation cycle (n≥2)

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

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

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

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

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

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

597   (15)

598

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

600

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

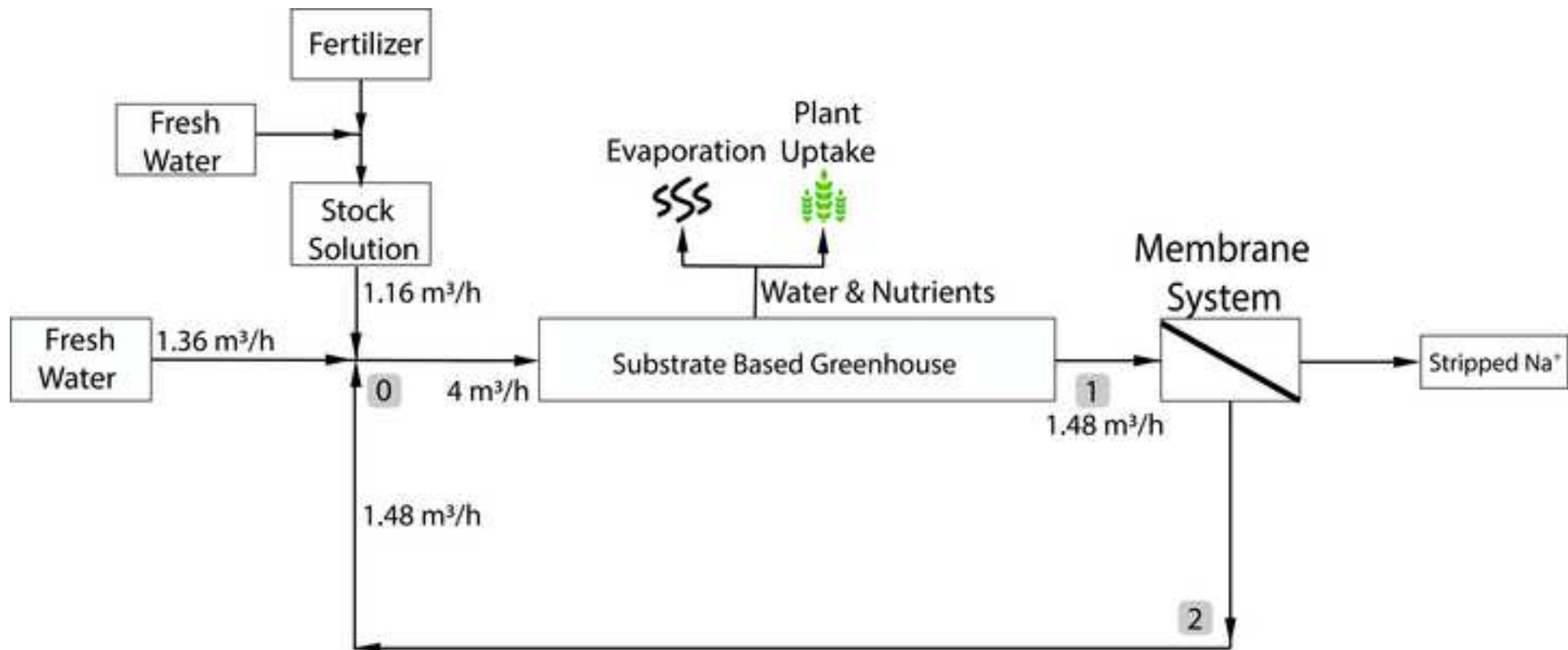602   (16)
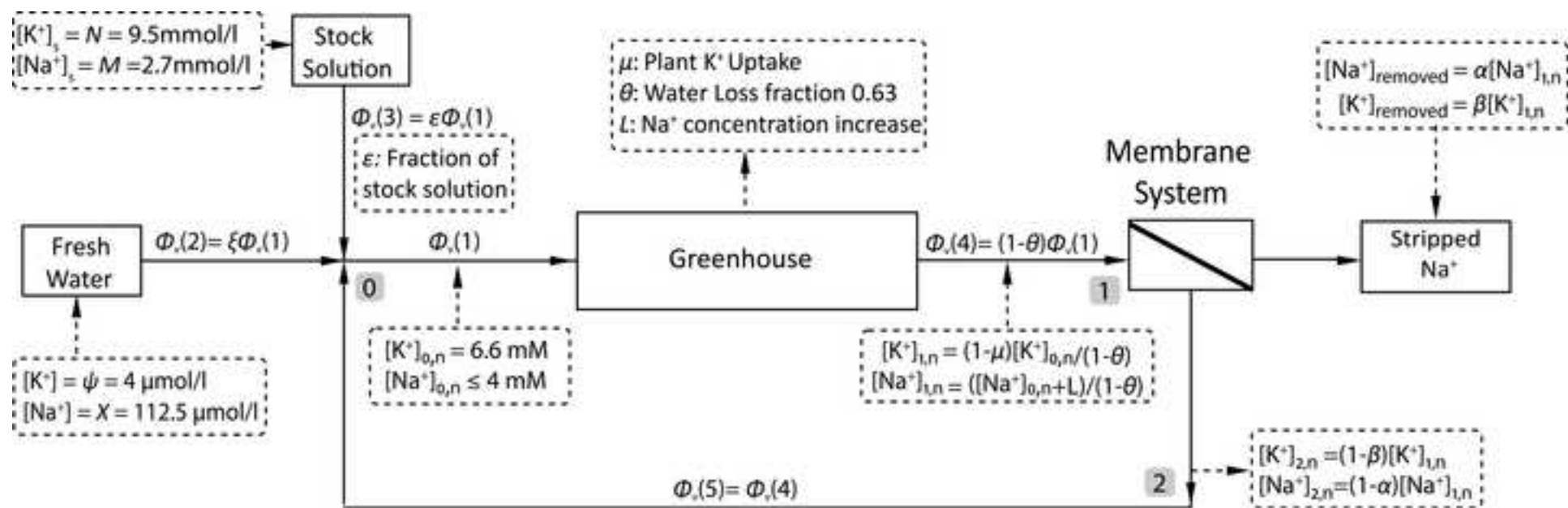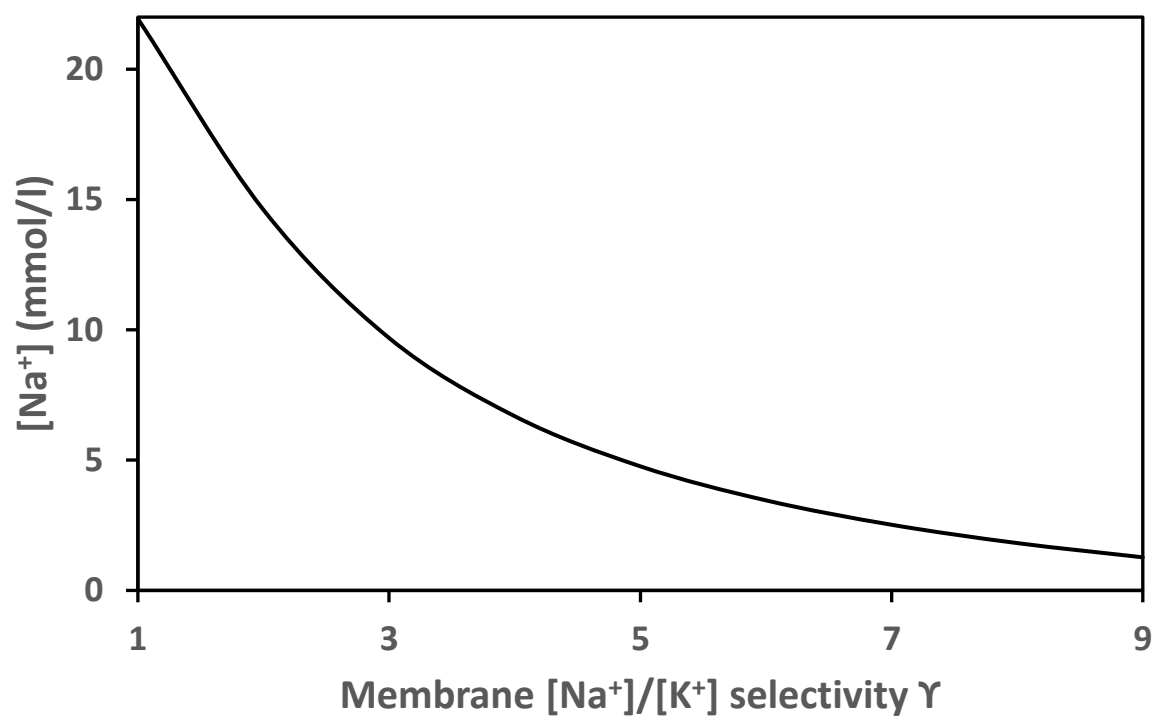
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604

Figure 1

Figure 2

$[K^+]_s = N = 9.5\,mmol/l$
$[Na^+]_s = M = 2.7\,mmol/l$

Stock Solution

μ: Plant K^+ Uptake
θ: Water Loss fraction 0.63
L: Na^+ concentration increase

$[Na^+]_{removed} = \alpha[Na^+]_{1,n}$
$[K^+]_{removed} = \beta[K^+]_{1,n}$

$\Phi_v(3) = \varepsilon\Phi_v(1)$

ε: Fraction of stock solution

Membrane System

$\Phi_v(2) = \xi\Phi_v(1)$

$\Phi_v(1)$

$\Phi_v(4) = (1-\theta)\Phi_v(1)$

Fresh Water

Greenhouse

Stripped Na^+

0

1

$[K^+] = \psi = 4\,\mu mol/l$
$[Na^+] = X = 112.5\,\mu mol/l$

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

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

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

2

$\Phi_v(5) = \Phi_v(4)$

Figure 3

Figure 4

Table

Variables		Values
$\Phi_v(1)$	Volumetric flow entering the greenhouse	4 m³/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 Φv(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.