

Supporting information for

**Blended Fertiliser as Draw Solutions for the Fertiliser Drawn Forward
Osmosis Desalination**

Sherub Phuntsho^a, Ho Kyong Shon^{a*}, Tahir Majeed^a, Ibrahim El Saliby^a, Saravanamuthu Vigneswaran^a, Jaya Kandasamy^a, Seungkwan Hong^b, Sangyoun Lee^b

^aSchool of Civil and Environmental Engineering, University of Technology, Sydney (UTS), Post Box 129, Broadway, NSW 2007, Australia.

^bSchool of Civil, Environmental & Architectural Engineering, Korea University, 1, 5-ka, Anam-Dong, Sungbuk-Gu, Seoul 136-713, Republic of Korea

* Corresponding author: Email: Hokyong.Shon-1@uts.edu.au

Total pages: 10 excluding cover page

Total Figures: 4

Total Tables: 2

SUPPORTING INFORMATION

S1. Forward osmosis experimental procedures

The performance of the FO process was conducted using lab scale FO unit, with similar features described elsewhere (Phuntsho *et al.*, 2011). The commercial FO membrane (Membrane 090128-NW-1, Hydration Technologies Inc., USA) was used which is made from cellulose acetate embedded in a polyester woven mesh and its characteristics are widely reported (McCutcheon *et al.*, 2005; Cath *et al.*, 2006; Tang *et al.*, 2010). The pure water permeability coefficient of the FO membrane was $A = 0.28194 \pm 0.008 \mu\text{m s}^{-1}\text{atm}^{-1}$. The coefficient was determined in RO mode at various hydraulic pressures using DI water as feed. The schematic layout of the FO experimental set up is shown in Figure S1.

The DS consisted of either 1.0 M single fertiliser or a blended solution of two or more fertilisers mixed in specific molar proportions. The performances of the DS was comparatively studied using DI water and brackish water or BW (5,000 mg/L) as feed as in other studies (Achilli *et al.*, 2010; Phuntsho *et al.*, 2011). The crossflow was run in a counter-current mode, since the water flux is slightly higher in this conditions (Mi and Elimelech, 2008). Both the feed and DS were supplied at crossflow velocities of 8.5 cm s^{-1} . The temperature of the feed and DS in all cases was maintained at 25°C . Water flux was measured continuously by connecting DS to a digital mass scale connected to a computer. Each experiment was carried out at least for six hours duration for effective monitoring of the reverse diffusion of draw solutes. When single fertiliser compound was used, reverse solute flux was monitored by recording electrical conductivity (EC) online using a multimeter (CP-500L, ISTEK) with separate probes attached and, connected to a computer for data logging. When blended fertiliser DS was used, reverse solute flux was measured by collecting and analysing the feed water samples at the end of each experiment. Total phosphorous and total nitrogen in the samples were analysed as per APHA 4500 standard while potassium was analysed using ICP-MS (Perkin Elmer Elan DRC-e). Membrane transport parameters such as the pure water permeability coefficient 'A' of FO membrane was evaluated using the methods described elsewhere (Phuntsho *et al.*, 2011).

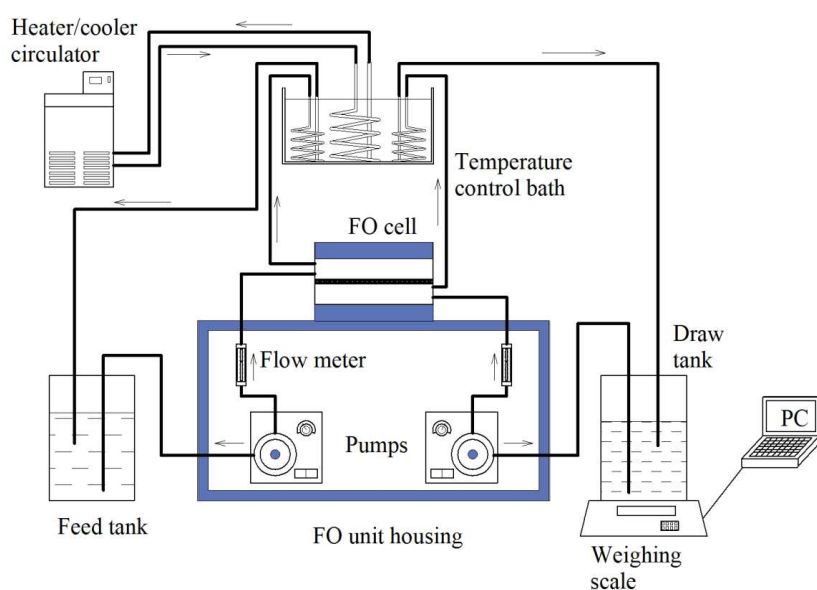


Figure S1: Schematic layout of the lab scale forward osmosis experimental set up

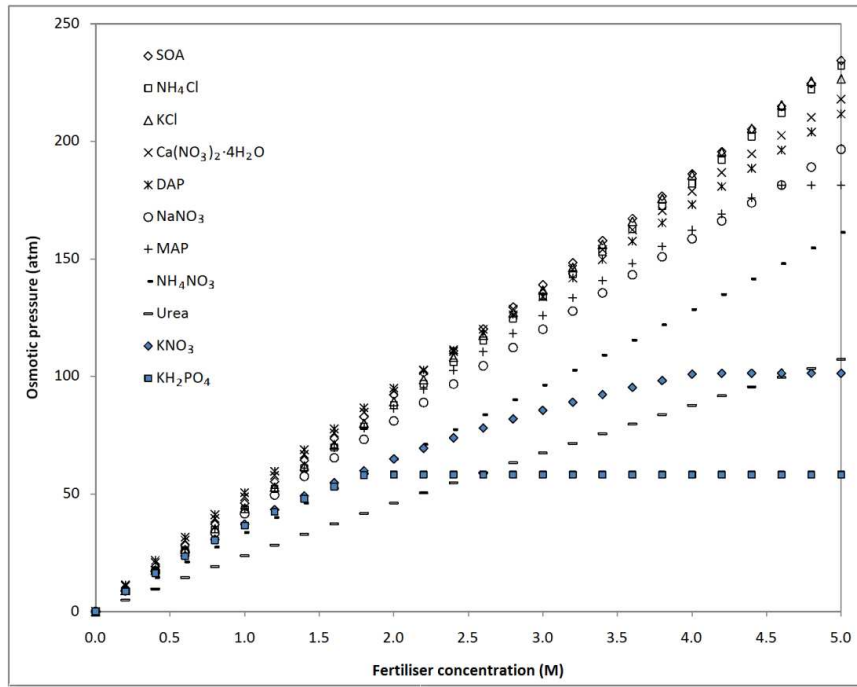


Figure S2. Osmotic pressure of fertiliser DS as a function of molar concentrations. Osmotic pressure was predicted using OLI Stream Analyser 3.1 (OLI Inc, USA) at 25°C.

S2 Determination of osmotic equilibrium in FO process experimentally

In order to determine the DS concentrations (or the bulk osmotic pressure) at which the water flux reaches zero or near zero, experiments were conducted at different low DS concentrations using BW (5,000 mg/L NaCl) as feed. Two types of DS were selected for the experiments: KCl (containing only monovalent ions) and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (containing both mono and divalent ions) and the water fluxes are plotted against the bulk osmotic pressure of the DS as shown in Figure S3. From the figure it is clear that, at low DS concentrations, the water flux in FO process becomes zero when the bulk osmotic pressure of the DS reaches osmotic equilibrium with the bulk osmotic pressure of the BW feed (i.e. $\pi_{D,b} = \pi_{F,b} = 3.9$ atm) irrespective of types of draw solutes used. This shows that, as the DS becomes more and more diluted due to influx of water from the feed water, the bulk osmotic pressure of the DS decreases thereby reducing the net driving force and ultimately the water flux across the membrane. At low water flux, the CP effects are also comparatively low and if the process is allowed to continue, the osmotic process can continue until the bulk osmotic pressures of the DS and the FS becomes equal (osmotic equilibrium).

However, in reality it may not be economically viable for osmotic process to continue using DS concentration below certain level because the cost of energy for pumping the DS and FS would far outweigh the amount of water it can extract within a specific time. An optimum initial DS concentration could be determined based on the total membrane area in a single membrane module arrays and the feed salinity concentrations.

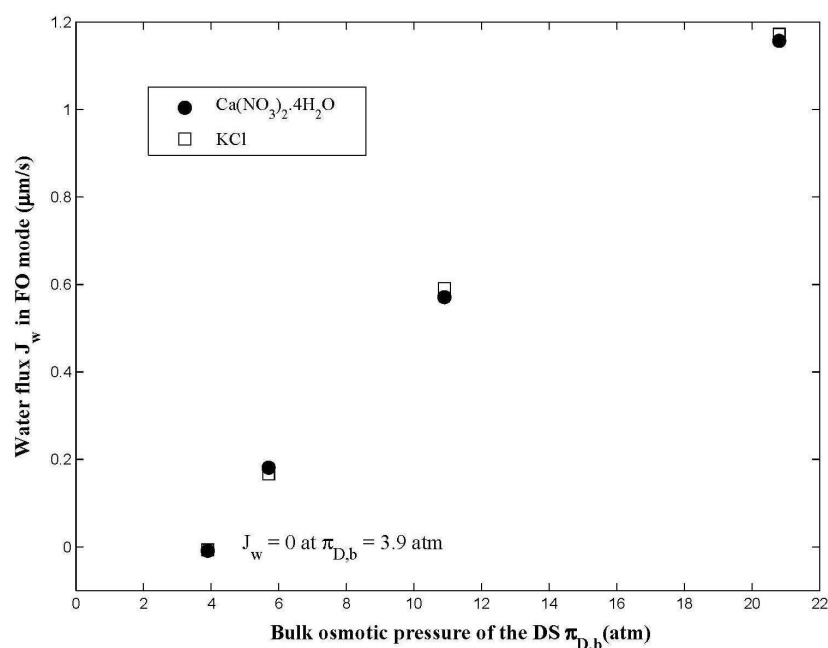


Figure S3. Variation of water flux in FO process at low DS concentrations or bulk osmotic pressure. The water flux at $\pi_{D,b}=3.9$ atm was zero.

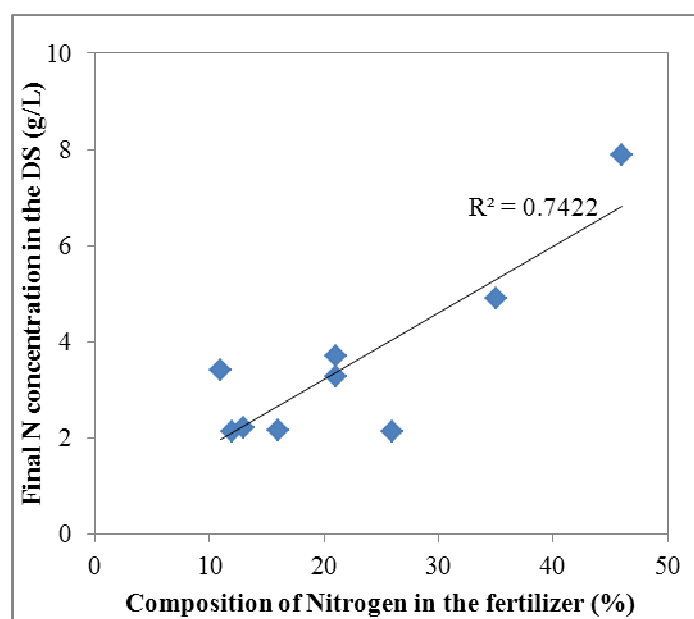


Figure S4: Comparison between % of N composition of N containing fertilisers and the N nutrient concentration in the final DS or desalted water with brackish water as feed water.

S3. Properties of the blended fertiliser draw solutions

Table S1 shows the pH and the osmotic pressure of the blended fertilisers DS. Most of the selected fertilisers could blend with each other and only few combinations resulted in the formation of precipitates especially when calcium containing fertilisers were blended with sulphate or phosphate fertilisers. For example, $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}(\text{NO}_3)_2$ blend resulted in the

formation of CaSO_4 (gypsum) precipitate while $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ and KH_2PO_4 with $\text{Ca}(\text{NO}_3)_2$ formed CaHPO_4 precipitates. Therefore these combinations are not suitable for fertiliser blending. Blending also decreased solubility of some fertilisers. For example, when $(\text{NH}_4)_2\text{SO}_4$ was blended with KCl , one of the products formed is K_2SO_4 which has much lower solubility than their original basic fertilisers (Imas, 1999). The decrease in the solubility could reduce the recovery rate at which FDFO desalination can operate because recovery rates depend on the fertiliser solubility. Higher fertiliser solubility leads to higher osmotic pressure for a particular fertiliser draw solution and therefore higher feed recovery rates are possible. The pH of all blended fertilisers in this study was within the range of pH 4.0 to 8.0, indicating that they are compatible with the commercially available cellulose acetate FO membrane.

When two different compounds were blended in the solution, the number and types of species formed varied depending on the type of fertiliser used. Speciation analysis using the OLI Stream Analyser indicated that urea was the only fertiliser that does not dissociate to form different species with any of the fertilisers blended at 25°C. Speciation is important because osmotic pressure is directly related to the number of species formed in the solution. While a number of species are important, the nature of the species is also important since non-charged species tend to diffuse more easily through the membrane.

In most blends, the osmotic pressure of the blended fertiliser solution was generally lower than the arithmetic sum of the osmotic pressures of the two individual fertiliser solutions, except for NH_4Cl blended with some fertilisers. For some fertiliser blends, the net osmotic pressure significantly decreased, while in some cases the decrease was minimal. For example, most fertilisers blended with KNO_3 and DAP resulted in lowering osmotic pressure in some cases by more than 10% with the highest reduction observed for KNO_3 and DAP blend at 22.6%. NH_4NO_3 with KH_2PO_4 and $\text{Ca}(\text{NO}_3)_2$ and, NH_4Cl with $\text{Ca}(\text{NO}_3)_2$ also decreased the net osmotic pressure by more than 10%. The reduction in the resultant osmotic pressure of the blended solution may be due to the change in the properties of the blended fertiliser solutions probably due to the formation of more complex species. Table S2 shows the comparative properties of KNO_3 and DAP and their blended solution as a typical example. When KNO_3 and DAP are blended (1 M : 1 M), the total number of species decreased to 4.45 M from 4.98 M for the combined species of the two different solutions and this has direct implications on the osmotic pressure. This blend also formed about 0.5 M of uncharged species (NH_4NO_3) which might played a role in lowering the osmotic pressure.

However, when NH_4Cl is blended with other fertilisers, the blended solution mostly resulted in increased osmotic pressure except when blended with urea, KNO_3 and $\text{Ca}(\text{NO}_3)_2$. The highest increase in osmotic pressure was observed for $(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{Cl}$ with about 10% increase. Urea has low osmotic pressure and therefore not suitable for use alone as DS. But when urea is blended with other fertilisers, there is no appreciable decrease in the net osmotic pressure except with $\text{Ca}(\text{NO}_3)_2$ and KNO_3 . This indicates that urea blended fertilisers can be used as DS for FO desalination and this is significant because, urea is one of the most commonly used N fertilisers in the world.

Table S1: Details of different fertilisers blended as draw solution for FDFO desalination using brackish water feed. MAP: Monoammonium phosphate - $\text{NH}_4\text{H}_2\text{PO}_4$, DAP: Diammonium phosphate $(\text{NH}_4)_2\text{HPO}_4$, SOA: sulphate of ammonia $(\text{NH}_4)_2\text{SO}_4$. A: Membrane permeability coefficient of the FO membrane determined in RO mode at different pressure using DI water $A = 0.28194 \pm 0.008 \mu\text{m s}^{-1}\text{atm}^{-1}$.

Fertiliser draw solution blends in 1M:1M (DS1+DS2)	Blended DS (pH)	Blended DS π (atm)	Sum of $\pi_1+\pi_2$ (atm)	M@3.9 atm	N/P/K concentrations in the final FDFO product water using BW as feed (g/L)			Actual Water Flux J_w ($\mu\text{m s}^{-1}$)			J_{wt} ($\mu\text{m s}^{-1}$)	Performance ratio (J_w/J_{wt} %)		
					DS1	DS2	Blended DS	DS1	DS2	Blended DS		DS1	DS2	Blended DS
Urea Blended Draw Solutions														
Urea+NH ₄ NO ₃	4.96	56.9	57.4	0.059	7.87/0/0	4.90/0/0	3.30/0/0	0.57	2.13	2.43	16.04	8.5	22.9	15.1
Urea+SOA	5.14	68.6	69.8	0.0491	7.87/0/0	3.70/0/0	2.75/0/0	0.57	1.99	2.16	19.34	8.5	14.4	11.2
Urea+MAP	4.2	66.2	67.5	0.0561	7.87/0/0	2.11/4.68/0	2.36/1.74/0	0.57	1.47	1.53	18.66	8.5	11.7	8.2
Urea + KCl	7	66.9	67.7	0.0561	7.87/0/0	0/0/5.9	1.57/0/2.19	0.57	2.57	3.21	18.86	8.5	20.4	17.0
Urea+KNO ₃	6.98	60	60.9	0.0566	7.87/0/0	2.20/0/6.14	2.38/0/2.21	0.57	1.87	2.83	16.91	8.5	12.5	16.8
Urea+KH ₂ PO ₄	4.19	59.2	60.2	0.0567	7.87/0/0	0/4.86/6.14	1.59/1.76/2.22	0.57	1.73	2.11	16.69	8.5	17.5	12.6
Urea+Ca(NO ₃) ₂	6.8	69.9	72.5	0.0468	7.87/0/0	3.39/0/0	2.62/0/0	0.57	2.15	2.05	19.70	8.5	14.9	10.4
Urea+NaNO ₃	7	64.4	65.2	0.0563	7.87/0/0	2.16/0/0	2.36/0/0	0.57	1.54	2.35	18.15	8.5	11.8	12.9
Urea+ DAP	7.8	73.2	74.3	0.046	7.87/0/0	3.28/3.62/0	2.58/1.43/0	0.57	1.79	2.03	20.64	8.5	11.2	9.8
Urea+NH ₄ Cl	4.8	66.2	67.2	0.0561	7.87/0/0	2.13/0/0	2.36/0/0	0.57	2.48	2.73	18.66	8.5	20.3	14.6
Ammonium Nitrate Blended Draw Solutions														
NH ₄ NO ₃ +Urea	4.96	56.9	57.4	0.059	7.87/0/0	4.90/0/0	3.30/0/0	2.13	0.57	2.43	16.04	22.9	8.5	15.1
NH ₄ NO ₃ +SOA	5.15	79.6	79.8	0.0363	3.7/0/0	4.90/0/0	2.03/0/0	2.13	1.99	2.96	22.44	22.9	14.4	13.2
NH ₄ NO ₃ +MAP	4.13	74.7	77.5	0.0457	2.11/4.68/0	4.90/0/0	1.92/1.42/0	2.13	1.47	2.86	21.06	22.9	11.7	13.6
NH ₄ NO ₃ +KCl	4.93	76.5	77.7	0.0448	0/0/5.9	4.90/0/0	1.25/0/1.75	2.13	2.57	3.53	21.57	22.9	20.4	16.4
NH ₄ NO ₃ +KNO ₃	5.06	66.6	70.9	0.0461	2.2/0/6.14	4.90/0/0	1.94/0/1.80	2.13	1.87	3.13	18.77	22.9	12.5	16.7
NH ₄ NO ₃ +KH ₂ PO ₄	7.74	78.5	70.2	0.045	0/4.86/6.14	4.90/0/0	1.26/1.40/1.76	2.13	1.73	2.81	22.13	22.9	17.5	12.7
NH ₄ NO ₃ +Ca(NO ₃) ₂	5.18	75.7	82.5	0.0415	3.39/0/0	4.90/0/0	2.32/0/0	2.13	2.15	3.33	21.34	22.9	14.9	15.6
NH ₄ NO ₃ +NaNO ₃	5.09	72.4	75.2	0.0459	2.16/0/0	4.90/0/0	1.93/0/0	2.13	1.54	3.16	20.41	22.9	11.8	15.5
NH ₄ NO ₃ +DAP	7.7	78.5	84.3	0.0406	3.28/3.62/0	4.90/0/0	2.27/1.26/0	2.13	1.79	3.68	22.13	22.9	11.2	16.6
NH ₄ NO ₃ +NH ₄ Cl	4.75	74.8	77.2	0.0457	4.9/0/0	2.13/0/0	1.92/0/0	2.13	2.48	3.95	21.09	22.9	20.3	18.7
Ammonium Sulphate Blended Draw Solutions														
SOA+Urea	5.14	68.6	69.8	0.0491	7.87/0/0	3.70/0/0	2.75/0/0	1.99	0.57	2.16	19.34	14.4	8.5	11.2
SOA+NH ₄ NO ₃	5.15	79.6	79.8	0.0363	3.7/0/0	4.90/0/0	2.03/0/0	1.99	2.13	2.96	22.44	14.4	22.9	13.2
SOA+MAP	4	89.6	89.9	0.041	3.7/0/0	2.11/4.68/0	1.72/1.27/0	1.99	1.47	2.09	25.26	14.4	11.7	8.3
SOA+KCl	5.1	89.6	90.1	0.0353	3.7/0/0	0/0/5.90	0.99/0/1.38	1.99	2.57	3.32	25.26	14.4	20.4	13.2
SOA+KNO ₃	5.28	70.2	83.3	0.0368	3.7/0/0	2.20/0/6.14	1.55/0/1.44	1.99	1.87	3.84	19.79	14.4	12.5	19.4
SOA+ KH ₂ PO ₄	4	75.1	82.6	0.043	3.7/0/0	0/4.86/6.14	1.20/1.33/1.68	1.99	1.73	2.83	21.17	14.4	17.5	13.4
SOA+ Ca(NO ₃) ₂														
SOA+NaNO ₃	5.3	83	87.6	0.035	3.7/0/0	2.16/0/0	1.47/0/0	1.99	1.54	3.44	23.40	14.4	11.8	14.7
SOA+DAP	7.6	95	96.7	0.0344	3.7/0/0	3.28/3.62/0	1.93/1.07/0	1.99	1.79	2.53	26.78	14.4	11.2	9.4
SOA+ NH ₄ Cl	5	98.5	89.6	0.0343	3.7/0/0	2.13/0/0	1.44/0/0	1.99	2.48	3.40	27.77	14.4	20.3	12.2
Monoammonium phosphate Blended Draw Solutions														
MAP + Urea	4.2	66.2	67.5	0.0561	7.87/0/0	2.11/4.68/0	2.36/1.74/0	1.47	0.57	1.53	18.66	11.7	8.5	8.2
MAP+NH ₄ NO ₃	4.13	74.7	77.5	0.0457	2.11/4.68/0	4.90/0/0	1.92/1.42/0	1.47	2.13	2.86	21.06	11.7	22.9	13.6
MAP+SOA	4	89.6	89.9	0.041	3.7/0/0	2.11/4.68/0	1.72/1.27/0	1.47	1.99	2.09	25.26	11.7	14.4	8.3
MAP+KCl	4.1	82.6	87.8	0.0436	2.11/4.68/0	0/0/5.90	0.61/1.35/1.7	1.47	2.57	3.42	23.28	11.7	20.4	14.7
MAP+KNO ₃	4.12	69.6	81	0.045	2.11/4.68/0	2.20/0/6.14	1.26/1.40/1.76	1.47	1.87	2.79	19.62	11.7	12.5	14.2
MAP+ KH ₂ PO ₄	4.05	75.5	80.3	0.0438	2.11/4.68/0	0/4.86/6.14	0.61/2.72/1.71	1.47	1.73	2.28	21.29	11.7	17.5	10.7
MAP+ Ca(NO ₃) ₂					Precipitation occurs									
MAP+NaNO ₃	4.07	77.1	85.3	0.0447	2.11/4.68/0	2.16/0/0	1.25/1.39/0	1.47	1.54	3.04	21.73	11.7	11.8	14.0

MAP+DAP	6	83.5	94.4	0.0391	2.11/4.68/0	3.28/3.62/0	1.64/2.42/0	1.47	1.79	2.21	23.54	11.7	11.2	9.4
MAP+ NH ₄ Cl	4.04	88.5	87.3	0.0433	2.11/4.68/0	2.13/0/0	1.21/1.34/0	1.47	2.48	3.21	24.95	11.7	20.3	12.8
Potassium Chloride Blended Draw Solutions														
KCl+Urea	7	66.9	67.7	0.0561	7.87/0/0	0/0/5.9	1.57/0/2.19	2.57	0.57	3.21	18.86	20.4	8.5	17.0
KCl+NH ₄ NO ₃	4.93	76.5	77.7	0.0448	0/0/5.9	4.90/0/0	1.25/0/1.75	2.57	2.13	3.53	21.57	20.4	22.9	16.4
KCl+SOA	5.1	89.6	90.1	0.0353	3.7/0/0	0/0/5.90	0.99/0/1.38	2.57	1.99	3.32	25.26	20.4	14.4	13.2
KCl+MAP	4.1	82.6	87.8	0.0436	2.11/4.68/0	0/0/5.90	0.61/1.35/1.7	2.57	1.47	3.42	23.28	20.4	11.7	14.7
KCl+KNO ₃	6.95	77.1	81.2	0.0437	0/0/5.9	2.2/0/6.14	0.61/1.35/3.42	2.57	1.87	2.53	21.73	20.4	12.5	11.6
KCl+ KH ₂ PO ₄	4.07	76.1	80.5	0.0438	0/0/5.9	0/4.86/6.14	0/1.36/3.43	2.57	1.73	3.34	21.45	20.4	17.5	15.6
KCl+ Ca(NO ₃) ₂	6.76	95.6	92.8	0.0326	0/0/5.9	3.39/0/0	0.91/0/1.27	2.57	2.15	3.08	26.95	20.4	14.9	11.4
KCl+NaNO ₃	6.97	83.7	85.5	0.0435	0/0/5.9	2.16/0/0	0.61/0/1.70	2.57	1.54	3.16	23.60	20.4	11.8	13.4
KCl+DAP	7.8	79.7	94.6	0.039	0/0/5.9	3.28/3.62/0	1.09/1.21/1.52	2.57	1.79	3.34	22.47	20.4	11.2	14.9
KCl+ NH ₄ Cl	4.8	88.6	87.5	0.0433	0/0/5.9	2.13/0/0	0.61/0/1.69	2.57	2.48	3.71	24.98	20.4	20.3	14.9
Potassium Nitrate Blended Draw Solutions														
KNO ₃ +Urea	6.98	60	60.9	0.0566	7.87/0/0	2.20/0/6.14	2.38/0/2.21	1.87	0.57	2.83	16.91	12.5	8.5	16.8
KNO ₃ +NH ₄ NO ₃	5.06	66.6	70.9	0.0461	2.2/0/6.14	4.90/0/0	1.94/0/1.80	1.87	2.13	3.13	18.77	12.5	22.9	16.7
KNO ₃ +SOA	5.28	70.2	83.3	0.0368	3.7/0/0	2.20/0/6.14	1.55/0/1.44	1.87	1.99	3.84	19.79	12.5	14.4	19.4
KNO ₃ +MAP	4.12	69.6	81	0.045	2.11/4.68/0	2.20/0/6.14	1.26/1.40/1.76	1.87	1.47	2.79	19.62	12.5	11.7	14.2
KNO ₃ +KCl	6.95	77.1	81.2	0.0437	0/0/5.9	2.2/0/6.14	0.61/1.35/3.42	1.87	2.57	2.53	21.73	12.5	20.4	11.6
KNO ₃ + KH ₂ PO ₄	4.1	63.9	73.7	0.0442	2.2/0/6.14	0/4.86/6.14	0.62/1.37/3.46	1.87	1.73	3.13	18.01	12.5	17.5	17.4
KNO ₃ + Ca(NO ₃) ₂	6.8	86	86	0.0329	2.2/0/6.14	3.39/0/0	1.38/0/1.29	1.87	2.15	3.23	24.24	12.5	14.9	13.3
KNO ₃ +NaNO ₃	6.97	73	78.7	0.0439	2.2/0/6.14	2.16/0/0	1.23/0/1.72	1.87	1.54	2.61	20.58	12.5	11.8	12.7
KNO ₃ +DAP	7.89	68	87.8	0.0404	2.2/0/6.14	3.28/3.62/0	1.70/1.25/1.58	1.87	1.79	3.41	19.17	12.5	11.2	17.8
KNO ₃ +NH ₄ Cl	4.93	76.5	80.7	0.0448	2.2/0/6.14	2.13/0/0	1.25/0/1.75	1.87	2.48	3.39	21.57	12.5	20.3	15.7
Potassium Dihydrogen Phosphate Blended Draw Solutions														
KH ₂ PO ₄ +Urea	4.19	59.2	60.2	0.0567	7.87/0/0	0/4.86/6.14	1.59/1.76/2.22	1.73	0.57	2.11	16.69	17.5	8.5	12.6
KH ₂ PO ₄ +NH ₄ NO ₃	7.74	78.5	70.2	0.045	0/4.86/6.14	4.90/0/0	1.26/1.40/1.76	1.73	2.13	2.81	22.13	17.5	22.9	12.7
KH ₂ PO ₄ +SOA	4	75.1	82.6	0.043	3.7/0/0	0/4.86/6.14	1.20/1.33/1.68	1.73	1.99	2.83	21.17	17.5	14.4	13.4
KH ₂ PO ₄ +MAP	4.05	75.5	80.3	0.0438	2.11/4.68/0	0/4.86/6.14	0.61/2.72/1.71	1.73	1.47	2.28	21.29	17.5	11.7	10.7
KH ₂ PO ₄ +KCl	4.07	76.1	80.5	0.0438	0/0/5.9	0/4.86/6.14	0/1.36/3.43	1.73	2.57	3.34	21.45	17.5	20.4	15.6
KH ₂ PO ₄ +KNO ₃	4.1	63.9	73.7	0.0442	2.2/0/6.14	0/4.86/6.14	0.62/1.37/3.46	1.73	1.87	3.13	18.01	17.5	12.5	17.4
KH ₂ PO ₄ + Ca(NO ₃) ₂														
KH ₂ PO ₄ +NaNO ₃	4.05	73.2	78	0.0439	0/4.86/6.14	2.16/0/0	0.61/1.36/1.72	1.73	1.54	1.52	20.64	17.5	11.8	7.4
KH ₂ PO ₄ +DAP	6.14	74.7	87.1	0.0393	0/4.86/6.14	3.28/3.62/0	1.10/2.44/1.54	1.73	1.79	2.45	21.06	17.5	11.2	11.6
KH ₂ PO ₄ + NH ₄ Cl	4.06	82.6	80	0.0436	0/4.86/6.14	2.13/0/0	0.61/1.35/1.70	1.73	2.48	3.18	23.28	17.5	20.3	13.6
Calcium Nitrate Blended Draw Solutions														
Ca(NO ₃) ₂ +Urea	6.8	69.9	72.5	0.0468	7.87/0/0	3.39/0/0	2.62/0/0	2.15	0.57	2.05	19.70	14.9	8.5	10.4
Ca(NO ₃) ₂ +NH ₄ NO ₃	5.18	75.7	82.5	0.0415	3.39/0/0	4.90/0/0	2.32/0/0	2.15	2.13	3.33	21.34	14.9	22.9	15.6
Ca(NO ₃) ₂ +SOA								Precipitation occurs						
Ca(NO ₃) ₂ +MAP								Precipitation occurs						
Ca(NO ₃) ₂ +KCl	6.76	95.6	92.8	0.0326	0/0/5.9	3.39/0/0	0.91/0/1.27	2.15	2.57	3.08	26.95	14.9	20.4	11.4
Ca(NO ₃) ₂ +KNO ₃	6.8	86	86	0.0329	2.2/0/6.14	3.39/0/0	1.38/0/1.29	2.15	1.87	3.23	24.24	14.9	12.5	13.3
Ca(NO ₃) ₂ +KH ₂ PO ₄								Precipitation occurs						
Ca(NO ₃) ₂ + NaNO ₃	6.81	96.8	90.3	0.0326	3.39/0/0	2.16/0/0	1.37/0/0	2.15	1.54	2.89	27.29	14.9	11.8	10.6
Ca(NO ₃) ₂ + DAP								Precipitation occurs						
Ca(NO ₃) ₂ +NH ₄ Cl	5.07	82	92.3	0.0407	3.39/0/0	2.13/0/0	1.71/0/0	2.15	2.48	3.62	23.12	14.9	20.3	15.6
Sodium Nitrate Blended Draw Solutions														
NaNO ₃ +Urea	7	64.4	65.2	0.0563	7.87/0/0	2.16/0/0	2.36/0/0	1.54	0.57	2.35	18.15	11.8	8.5	12.9
NaNO ₃ +NH ₄ NO ₃	5.09	72.4	75.2	0.0459	2.16/0/0	4.90/0/0	1.93/0/0	1.54	2.13	3.16	20.41	11.8	22.9	15.5
NaNO ₃ +SOA	5.3	83	87.6	0.035	3.7/0/0	2.16/0/0	1.47/0/0	1.54	1.99	3.44	23.40	11.8	14.4	14.7

NaNO ₃ +MAP	4.07	77.1	85.3	0.0447	2.11/4.68/0	2.16/0/0	1.25/1.39/0	1.54	1.47	3.04	21.73	11.8	11.7	14.0
NaNO ₃ +KCl	6.97	83.7	85.5	0.0435	0/0/5.9	2.16/0/0	0.61/0/1.70	1.54	2.57	3.16	23.60	11.8	20.4	13.4
NaNO ₃ +KNO ₃	6.97	73	78.7	0.0439	2.2/0/6.14	2.16/0/0	1.23/0/1.72	1.54	1.87	2.61	20.58	11.8	12.5	12.7
NaNO ₃ +KH ₂ PO ₄	4.05	73.2	78	0.0439	0/4.86/6.14	2.16/0/0	0.61/1.36/1.72	1.54	1.73	1.52	20.64	11.8	17.5	7.4
NaNO ₃ +Ca(NO ₃) ₂	6.81	96.8	90.3	0.0326	3.39/0/0	2.16/0/0	1.37/0/0	1.54	2.15	2.89	27.29	11.8	14.9	10.6
NaNO ₃ +DAP	7.84	50.7	92.1	0.0403	2.16/0/0	3.28/3.62/0	1.69/1.25/0	1.54	1.79	2.26*	14.29	11.8	11.2	15.8
NaNO ₃ + NH ₄ Cl	4.95	81.5	85	0.0446	2.16/0/0	2.13/0/0	1.25/0/0	1.54	2.48	3.38	22.97	11.8	20.3	14.7
Diammonium Phosphate Blended Draw Solutions														
DAP+Urea	7.8	73.2	74.3	0.046	7.87/0/0	3.28/3.62/0	2.58/1.43/0	1.79	0.57	2.03	20.64	11.2	8.5	9.8
DAP+NH ₄ NO ₃	7.7	78.5	84.3	0.0406	3.28/3.62/0	4.90/0/0	2.27/1.26/0	1.79	2.13	3.68	22.13	11.2	22.9	16.6
DAP+SOA	7.6	95	96.7	0.0344	3.7/0/0	3.28/3.62/0	1.93/1.07/0	1.79	1.99	2.53	26.78	11.2	14.4	9.4
DAP+MAP	6	83.5	94.4	0.0391	2.11/4.68/0	3.28/3.62/0	1.64/2.42/0	1.79	1.47	2.21	23.54	11.2	11.7	9.4
DAP+KCl	7.8	79.7	94.6	0.039	0/0/5.9	3.28/3.62/0	1.09/1.21/1.52	1.79	2.57	3.34	22.47	11.2	20.4	14.9
DAP+KNO ₃	7.89	68	87.8	0.0404	2.2/0/6.14	3.28/3.62/0	1.70/1.25/1.58	1.79	1.87	3.41	19.17	11.2	12.5	17.8
DAP+KH ₂ PO ₄	6.14	74.7	87.1	0.0393	0/4.86/6.14	3.28/3.62/0	1.10/2.44/1.54	1.79	1.73	2.45	21.06	11.2	17.5	11.6
DAP+Ca(NO ₃) ₂	Precipitation occurs													
DAP+NaNO ₃	7.84	50.7	92.1	0.0403	2.16/0/0	3.28/3.62/0	1.69/1.25/0	1.79	1.54	2.26*	14.29	11.2	11.8	15.8
DAP+ NH ₄ Cl	7.67	89.4	94.1	0.0389	3.28/3.62/0	2.13/0/0	1.63/1.21/0	1.79	2.48	3.16	25.20	11.2	20.3	12.5
Ammonium Nitrate Blended Draw Solutions														
NH ₄ Cl +Urea	4.8	66.2	67.2	0.0561	7.87/0/0	2.13/0/0	2.36/0/0	2.48	0.57	2.73	18.66	20.3	8.5	14.6
NH ₄ Cl +NH ₄ NO ₃	4.75	74.8	77.2	0.0457	4.9/0/0	2.13/0/0	1.92/0/0	2.48	2.13	3.95	21.09	20.3	22.9	18.7
NH ₄ Cl +SOA	5	98.5	89.6	0.0343	3.7/0/0	2.13/0/0	1.44/0/0	2.48	1.99	3.40	27.77	20.3	14.4	12.2
NH ₄ Cl +MAP	4.04	88.5	87.3	0.0433	2.11/4.68/0	2.13/0/0	1.21/1.34/0	2.48	1.47	3.21	24.95	20.3	11.7	12.8
NH ₄ Cl +KCl	4.8	88.6	87.5	0.0433	0/0/5.9	2.13/0/0	0.61/0/1.69	2.48	2.57	3.71	24.98	20.3	20.4	14.9
NH ₄ Cl +KNO ₃	4.93	76.5	80.7	0.0448	2.2/0/6.14	2.13/0/0	1.25/0/1.75	2.48	1.87	3.39	21.57	20.3	12.5	15.7
NH ₄ Cl +KH ₂ PO ₄	4.06	82.6	80	0.0436	0/4.86/6.14	2.13/0/0	0.61/1.35/1.70	2.48	1.73	3.18	23.28	20.3	17.5	13.6
NH ₄ Cl +Ca(NO ₃) ₂	5.07	82	92.3	0.0407	3.39/0/0	2.13/0/0	1.71/0/0	2.48	2.15	3.62	23.12	20.3	14.9	15.6
NH ₄ Cl +NaNO ₃	4.95	81.5	85	0.0446	2.16/0/0	2.13/0/0	1.25/0/0	2.48	1.54	3.38	22.97	20.3	11.8	14.7
NH ₄ Cl +DAP	7.67	89.4	94.1	0.0389	3.28/3.62/0	2.13/0/0	1.63/1.21/0	2.48	1.79	3.16	25.20	20.3	11.2	12.5

*experiment conducted at DS concentration of (0.625 M : 0.625 M) since at 1 M:1 M, the blend was not easily soluble.

Table S2: Comparative properties of KNO₃, DAP and KNO₃+DAP fertiliser solutions

Properties	KNO ₃	(NH ₄) ₂ HPO ₄	Blended (1 M :1 M)
pH	6.970	7.780	7.890
Osmotic pressure (atm)	37.190	50.560	68.030
Ionic strength (mol/mol)	0.017	0.051	0.058
EC (mS/cm)	89.729	137.073	140.397
K ⁺ (mol)	1.000		1.000
NO ₃ ⁻ (mol)	1.000		0.506
NH ₃ aqueous (mol)	0.026		
NH ₄ ⁺ (mol)		1.974	1.483
P ₂ O ₇ ⁴⁻ (mol)		0.011	
HPO ₄ ³⁻ (mol)		0.947	0.965
H ₂ PO ₄ ⁻ (mol)		0.021	
NH ₄ NO ₃ (aqueous) (mol)			0.494
Total charged species (mol)	2.000	2.952	3.950
Total uncharged species (mol)	0.026	NIL	0.494
Total species (mol)	2.026	2.952	4.448

S4. Explanations on the performance of certain blended fertiliser draw solutions

The decrease or increase in water flux for the blended fertilisers is explained below. Using DI water as feed water (bulk osmotic pressure of the feed is zero), the actual or experimental water flux J_w in FO mode is given by the following equation (McCutcheon and Elimelech, 2006; McCutcheon and Elimelech, 2007), which takes into account the influence of internal concentration polarisation (ICP) on the DS side facing the porous support layer of the membrane.

$$J_w = A\sigma[\pi_d \exp(-J_w K)] \quad (S1)$$

Where A is the pure water permeability coefficient, π_d is the bulk osmotic pressure of the DS, σ the reflection coefficient (considered $\sigma = 1$ in this case) and K the solute resistance to diffusion within the membrane support layer. K is in fact a measure of how easily a draw solute can diffuse into or out of the membrane support layer and thus measures the severity of ICP (McCutcheon and Elimelech, 2006; McCutcheon and Elimelech, 2007). K is given by the following equation:

$$K = \frac{t\tau}{D\varepsilon} \quad (S2)$$

Where t , τ and ε are all related to the structural properties of the membrane such as thickness, tortuosity and porosity of the membrane support layer and, D the diffusion coefficient of the draw solutes. Since all the experiments were performed using the same membrane, the performance of each DS is a function of K which in turn is a function of diffusion coefficient of the draw solutes from equation (1) and (2). Therefore, blending different fertilisers would not only alter the types of species formed in the solution but the coexistence of different species could also alter the diffusivity of a particular species.

Blended fertiliser solutions have multiple component species in comparison to basic fertiliser solutions. For concentrated solutions and solutions containing multiple component species,

the diffusion coefficients are difficult to estimate because the solution does not obey the binary form of Fick's law however one of the exceptions is the mixture of weak electrolytes (Cussler, 2007). Urea being a weak electrolyte in this study, has been chosen as a typical example to explain the variations of flux and reverse diffusion of draw solutes in the blended draw solution.

For example, the average diffusion coefficient of KNO_3 in 1 M pure solution is $1.784 \times 10^{-9} \text{ m}^2/\text{s}$ however, its diffusion coefficient increases to $1.927 \times 10^{-9} \text{ m}^2/\text{s}$ in the urea+ KNO_3 blended solution. The diffusion coefficient of urea did not alter significantly when blended with KNO_3 . Similarly, the average diffusion coefficient of NaNO_3 also increased from $1.4241 \times 10^{-9} \text{ m}^2/\text{s}$ to $1.519 \times 10^{-9} \text{ m}^2/\text{s}$ when blended with urea in the solution. The average diffusion coefficients were calculated using equations provided elsewhere (Cussler, 2007; Tan and Ng, 2008). The diffusion coefficients of each ionic species in the solution were determined by OLI Stream Analyser 3.2. This increase in the draw solute diffusivity helps in lowering the solute resistivity K (equation 2) and therefore decreasing the ICP effects on the porous side of the membrane thereby enhancing the water flux. ICP is one of the major factors responsible for limiting the water flux by FO process (Gray *et al.*, 2006; McCutcheon and Elimelech, 2006; Tan and Ng, 2008; Tang *et al.*, 2010; Wang *et al.*, 2010). Even at the same osmotic pressure, each type of DS has been observed to have different pure water flux indicating that, each type of DS offer different degree of ICP effects in the FO process (Achilli *et al.*, 2010; Phuntsho *et al.*, 2011). The degree of ICP is higher at higher DS concentration and due to reduced diffusivity of the draw solutes at higher concentration (Tan and Ng, 2008).

S5. References

- Achilli, A., Cath, T. Y. and Childress, A. E. (2010). Selection of inorganic-based draw solutions for forward osmosis applications. *Journal of Membrane Science* 364(1-2), 233-241.
- Cath, T. Y., Childress, A. E. and Elimelech, M. (2006). Forward osmosis: Principles, applications, and recent developments: Review. *Journal of Membrane Science* 281(2006), 70-87.
- Cussler, E. L. (2007). *Diffusion - mass transfer in fluid systems*. 3rd Ed. Cambridge University Press, Cambridge, UK.
- Gray, G. T., McCutcheon, J. R. and Elimelech, M. (2006). Internal concentration polarisation in forward osmosis: role of membrane orientation. *Desalination* 197(1-3), 1-8.
- Imas, P. (1999). Recent techniques in fertigation of horticultural crops in Israel. IPI-PRII-KKV workshop on recent trends in nutritional management in horticultural crops. 11-12 Feb 1999. Dapoli, Maharashtra, India.
- McCutcheon, J. R. and Elimelech, M. (2006). Influence of concentrative and dilutive internal concentration polarisation on flux behavior in forward osmosis. *Journal of Membrane Science* 284(1-2), 237-247.
- McCutcheon, J. R. and Elimelech, M. (2007). Modelling water flux in forward osmosis: implications for improved membrane design. *AIChE* 53(7), 1736-1744.
- McCutcheon, J. R., McGinnis, R. L. and Elimelech, M. (2005). A novel ammonia-carbon dioxide forward (direct) osmosis desalination process. *Desalination* 174(2005), 1-11.
- Mi, B. and Elimelech, M. (2008). Chemical and physical aspects of organic fouling of forward osmosis membranes. *Journal of Membrane Science* 320(2008), 292-302.
- Phuntsho, S., Shon, H. K., Hong, S. K., Lee, S. Y. and Vigneswaran, S. (2011). A novel low energy fertiliser driven forward osmosis desalination for direct fertigation: evaluating the performance of fertiliser draw solutions. *J. Membr. Sci.* 375(2011), 172-181.
- Tan, C. H. and Ng, H. Y. (2008). Modified models to predict flux behavior in forward osmosis in consideration of external and internal concentration polarisations. *Journal of Membrane Science* 324(1-2), 209-219.

- Tang, C. Y., She, Q., Lay, W. C. L., Wang, R. and Fane, A. G. (2010). Coupled effects of internal concentration polarisation and fouling on flux behavior of forward osmosis membranes during humic acid filtration. *Journal of Membrane Science* 354(1-2), 123-133.
- Wang, K. Y., Ong, R. C. and Chung, T.-S. (2010). Double-Skinned Forward Osmosis Membranes for Reducing Internal Concentration Polarisation within the Porous Sublayer. *Industrial & Engineering Chemistry Research* 49(10), 4824-4831.