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Comment on Article

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A recent publication in *Energy & Environmental Science* by Metzger et al.[1] presented a techno-economic analysis of electrochemical water desalination technologies, specifically focusing on membrane capacitive deionization (MCDI), hybrid capacitive deionization (HCDI), and intercalative deionization (IDI). In their analysis, the authors predicted the capital investment as well as the operational costs, with the latter assumed to be based on the energy consumption of desalination. Ultimately, the study concludes that IDI is highly promising, largely based on the claim of superior energy efficiency with respect to other desalination technologies. However, the energy consumption analysis performed in this study is overly simplified, compromising the validity of the technological comparison. In this Comment, we discuss the issues in the applied method of comparing energy consumption among technologies and provide a corrected approach with new results for a more valid comparison.

The focus of our Comment is in regards to Figure 6 of the article, in which the authors show the "energy efficiency", $\hat{E}_{fresh}$, of multiple desalination technologies as a function of feedwater salt concentration. We note that the term "energy efficiency" is improperly utilized, with energy efficiency in the context of desalination processes typically referring to the second-law efficiency, which compares the actual energy consumption to the thermodynamic minimum energy consumption.[2-5] Rather, $\hat{E}_{fresh}$, defined as the energy spent per unit of freshwater produced, is more appropriately referred to as the specific energy consumption[6] for the remainder of the discussion.

Through Figure 6, the authors aim to compare the specific energy consumption of several desalination technologies across a wide range of feed concentrations. Particularly, salinities ranging from 100 ppm to 100,000 ppm NaCl are shown, encompassing the brackish water and seawater ranges. A critical shortcoming of Figure 6, however, is that the particular separation parameters for the presented data are not specified. To compare various desalination technologies fairly, the desalination separation parameters — namely, the feed salinity, extent of salt removal, and water recovery — must be held consistent, though in Figure 6, the authors provide only the feed salinity. Nonetheless, it can be inferred from the reported energy consumptions that the separation parameters are not unified across technologies. Such an approach is highly problematic since RO inherently removes extensive amounts of salt (>99%) across all feed salinities, whereas CDI-based technologies are generally operated with significantly lower salt removals, especially

when higher feed salinities are treated.[2, 7, 8] Hence, when the separation parameters are not held consistent, the energy consumption of RO would be inflated with respect to CDI, as it is used to perform a more "difficult" water-salt separation. Similarly, the productivity — the rate of water production per mass transfer area — must be fixed among the technologies to ensure valid comparison. Though the productivity does not directly affect the thermodynamic minimum energy requirement,[6] an increase in productivity generally demands a larger specific energy consumption to facilitate the increased rate of mass transfer.[9, 10] In Metzger et al., however, the productivity is not considered.

In addition to the nonunified separation parameters and productivity, it is important to note that the authors use overly simplified modeling techniques to predict the specific energy consumption of each technology. The energy consumption of RO is adapted from Urban[11] and Oren[12], which linearly extrapolate the specific energy consumption across the entire salinity range based on values from actual desalination plants that include additional energy-consuming processes such as intake, pre-treatment, and post-treatment.[13] Furthermore, energy recovery, despite being commonly practiced in RO, is not considered.[12]

The CDI modeling performed in Metzger et al. is also highly empirical, largely depending on the system geometry, internal resistance values, and cell voltage profiles (over a charge-discharge cycle) from only a few experimental studies conducted under particular operating conditions and separation parameters. Specifically, the authors calculate the energy consumption of each of the CDI processes according to (eq 18 in the original paper)

$$E_{charge} = I_{\text{charge}} \int_0^{t_{\text{charge}}} E_{\text{cell}} dt \quad (1)$$

where I_{charge} is the required current to achieve a given extent of salt removal, t_{charge} is the time of the charging step, and E_{cell} is the cell voltage.

For the I_{charge}, the authors assume a fixed charge efficiency value of 0.92. Though such a charge efficiency is reasonable for relatively low feed salinities and extents of salt removal,[4] the authors extend this value into their modeling of the entire brackish water and seawater regimes. The actual charge efficiency in CDI, however, is known to considerably vary with the feed salinity and the cell potential.[14, 15]

The authors also simplify the determination of E_{cell} and its time dependence by only taking the *iR* corrected voltage profiles from three experimental studies — one for each CDI technology (i.e., MCDI, HCDI, IDI). These voltage profiles are then extended across the entire feed salinity range according to the determined I_{charge} and the fixed internal resistance value, R_{mod}. The cell voltage in actual CDI operation, however, is highly dependent on several parameters including the feed salinity, extent of salt removal, salt removal rate, and electrode properties. Therefore, the approach taken by the authors is likely to lead to major error in the determination of energy consumption.

In addition, the modeling of energy recovery in Metzger et al., in which a fixed energy recovery ratio (ER) is utilized across all simulated separation parameters and operating conditions, is erroneous and overly simplified. It has been demonstrated that the fraction of potentially recoverable energy in MCDI is highly dependent on the internal cell resistances, the feed salinity and extent of salt removal, and the operating conditions during both the charge and discharge step (i.e., current density and flowrate).[16, 17]

As a result of the simplifying assumptions made by the authors, each of the CDI performance lines presented in Figure 6 show a simple linear trend across the entirety of the feed salinity range presented, though in actuality non-ideal transport phenomena such as concentration polarization and co-ion leakage lead to deviation from such behavior.[10, 18-20] Furthermore, without the specification of the separation parameters, which set the thermodynamic minimum energy consumption,[6] the presentation of a thermodynamic minimum energy consumption line is illogical. However, the authors show a line for the thermodynamic minimum energy consumption ($\hat{E}_{min}$), adapting it from values reported in previous studies, rather than properly calculating it for variable separation parameters.

Due to the abovementioned issues in the energy analysis performed by Metzger et al., the conclusions drawn in the article based on Figure 6 must be reevaluated. Particularly, the authors state that the energy consumption of MCDI is lower than RO and electrodialysis (ED) across the entire brackish water range, in direct contrast with the findings of previous works, which show RO and ED are considerably more energy efficient then MCDI for brackish water desalination.[2, 19, 20] Hence, in Figure 1 we present a revised version of Metzger et al.'s Figure 6 to demonstrate the vastly different results obtained upon correcting the described shortcomings of the energy analysis. Specifically, we show the specific energy consumption of RO, ED, and MCDI, as well as the

thermodynamic minimum energy consumption for various feed salinities. Notably, the separation parameters are specified and unified across all technologies by fixing the product water salinity for all feed salinities (i.e., the extent of salt removal), water recovery, and productivity at 500 ppm, 50%, and 15 L m^{-2} h^{-1}, respectively. Though we do not directly simulate the performance of HCDI and IDI, we reiterate that the modeling approach taken by the authors for HCDI and IDI is the same as MCDI;[1] thus, error in the MCDI data suggests similar issues in the validity of the shown HCDI and IDI results.

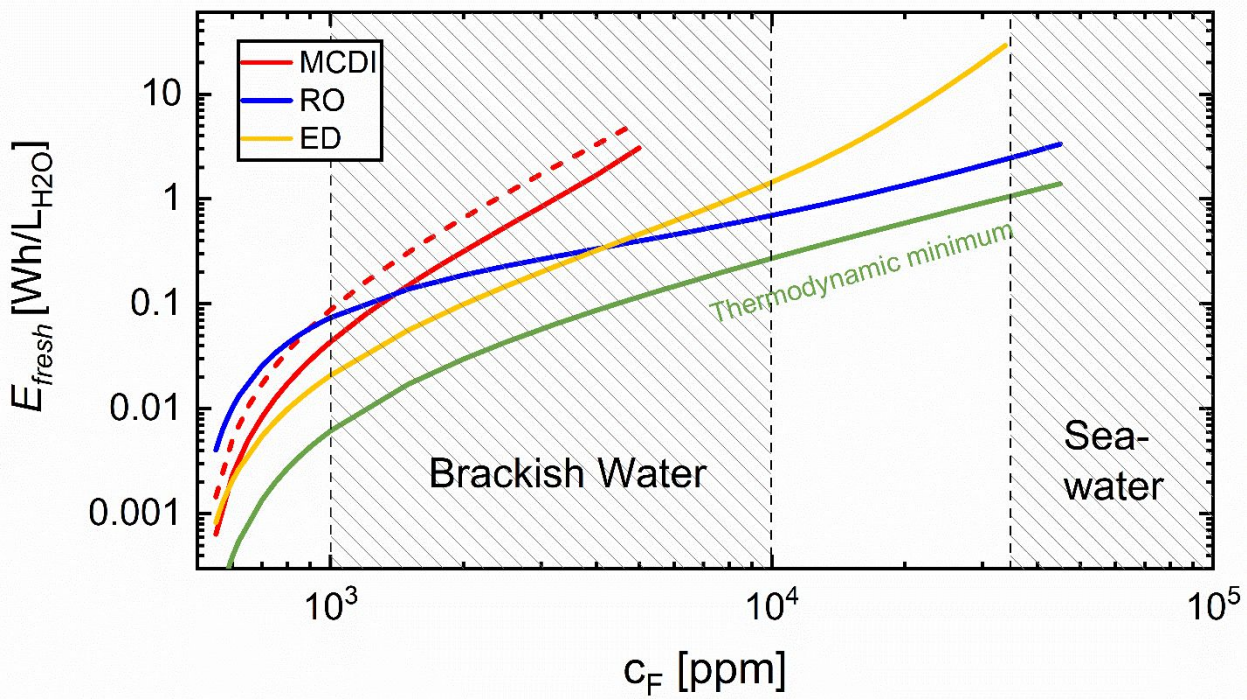

Figure 1. The specific energy consumption ($\hat{E}_{fresh}$) of desalination by MCDI (red), RO (blue), and ED (yellow) for varying feed salinities. The dashed red line indicates MCDI without energy recovery, whereas the solid line indicates the application of energy recovery with reverse current operation. The product water salinity is fixed at 500 ppm for all the feed salinities, while the water recovery and productivity are set at 50% and 15 L m^{-2} h^{-1}, respectively. The thermodynamic minimum energy requirement for each of the separation parameters is shown by the green line.

Since RO membranes inherently operate with very high salt rejection, here we utilize a bypass system, as introduced in our previous study,[19] in which only a portion of the feedwater is passed through the RO module — enabling variable salt removal for fair comparison with MCDI and ED. Feedwater which does not directly pass through the high-pressure pump and RO module is redirected to either a brine or product bypass stream. By mixing the product bypass stream with

the permeate from the RO module, the degree of salt removal can effectively be controlled. The flow rates of the three streams are numerically optimized for each set of separation parameters to minimize the specific energy consumption, using the module-scale water recovery as the variable parameter. As is commonly practiced in RO, we apply an energy recovery device to recoup energy stored in the retentate stream. Here, we assume an energy recovery device with 80% efficiency, a relatively conservative value with respect to current state of the art pressure-exchangers.[21, 22] Mass transfer modeling in the RO module is conducted using a classical solution-diffusion model, with film theory applied to describe concentration polarization. Specified parameters for the RO model can be found in Table 1 and further details regarding the RO bypass system modeling can be found in our previous work.[19]

We note that in Figure 1, the presented curve for RO is not entirely linear, in contrast to Figure 6 of Metzger et al., in which the RO data across the entire feed salinity range was simply linearly extrapolated.[12] Rather, because we employ a bypass system to achieve the necessary variable salt removal for each feed salinity, we obtain a curve in which the initial rate of increase of $\hat{E}_{fresh}$ for RO is high, eventually steadying off to a more linear relation for the treatment of higher feed salinities. This is a sensible result, as for low feed salinities (<1 g L^{-1}), the extent of salt removal required to achieve the fixed product water salinity (500 ppm) is small. Thus, most of the feedwater is bypassed away from the RO module, and any small increase in the feed salinity leads to a relatively large difference in the amount of water which must be directed to the RO module (which is directly proportional to the required hydraulic pressure and energy consumption). When treating feed salinities in the brackish water regime and beyond, in contrast, a sizeable portion of the feedwater must be sent through the RO module to achieve the 500 ppm product water requirement, making the trend (for a fixed product water salinity, productivity, and membrane water permeability coefficient) increasingly linear.

To determine the energy consumption of ED, we use a previously demonstrated two-dimensional Nernst-Planck modeling approach, thereby capturing the primary ion-transport mechanisms of the ED process.[20, 23-26] Specifically, the Nernst-Planck equation is numerically solved in both the spacer channel and ion-exchange membranes with the assumption of electroneutrality, allowing for the determination of the salt concentration and potential at each point in the ED stack. Such an approach to ED modeling captures the effects of non-ideal

phenomena which are prevalent at high feed salinities and extents of salt removal, such as the back-diffusion of ions from the concentrate channel to the diluate channel and the transport of co-ions across ion-exchange membranes. The ED system is operated in single-pass continuous flow mode, and assumed to be at steady state. ED modeling parameters utilized are shown in Table 1, and further detail regarding the calculation of energy consumption can be found in the literature.[20, 24]

In Figure 1, it can be seen that the $\hat{E}_{fresh}$ curve of ED shows varying behavior according to the feed salinity region. For feed salinities below the brackish water regime, the rate of change of $\hat{E}_{fresh}$ is highly variable. This is because at such low salt concentrations, the solutions in the spacer channels pose high electrical resistance. In our analysis, we fix the product water concentration at 500 ppm, but the salinity in the concentrate channel varies, increasing with the feedwater concentration. Thus, as the brackish water region is approached, the conductivity of the solution in the concentrate channels increases, in effect diminishing the contribution of the concentrate channel potential drop to the overall energy consumption. The rate of increase of $\hat{E}_{fresh}$, as a result, begins to decline (i.e., "level-off"). For the treatment of brackish water, a steady rate of growth in the energy consumption is observed, though when the feed salinity is further extended, the energy consumption begins to show exponential-like growth. This increased growth rate in $\hat{E}_{fresh}$ is the result of the growing severity of concentration polarization and the large concentration differences that develop across the ion-exchange membranes — both of which exacerbate the counterproductive phenomena of back-diffusion and co-ion leakage, and effectively deteriorate the current efficiency of desalination. We note that the $\hat{E}_{fresh}$ curve of ED does not extend into the seawater regime, as the high degrees of salt removal would require very large energy consumption and the application of current densities which exceed the practical limiting current density (i.e., the current density which leads to zero concentration at the membrane surface on the diluate-side due to concentration polarization) for such a single-stage operation.

Our modeling of MCDI, like ED, relies on the mechanistic description of ion-transport using the Nernst-Planck equation, in addition to modified Donnan theory to describe the structure of the electrical double layer. Such an approach is commonly adopted for MCDI modeling; hence, we refer the reader to the literature for further detail.[4, 15, 20, 27, 28] An MCDI cell is typically charged under either constant current (CC) or constant voltage (CV) operation.[29] In this analysis, we apply

CC charging, in which a constant current is applied during the charging step and the cell voltage increases over the charging duration, due to its advantage of achieving a consistent effluent salinity with respect to time. To achieve a reasonable separation, the charging duration is set to 300 s, and with the water recovery being fixed at 50% throughout our analysis, the discharging duration and flow rate are held equivalent to that of the charging step. Additional specified parameters for the MCDI modeling are provided in Table 1. Similar to Metzger et al., we consider the energy consumption of MCDI both with and without energy recovery, with the dashed line representing the application of energy recovery. We note that in our modeling, we rigorously calculate the recoverable energy for each simulated separation, rather than use a fixed recovery ratio as assumed by Metzger et al. Specifically, we calculate the recoverable energy in MCDI as the amount of energy stored in the electrical double layer over the charging step minus the unavoidable resistive losses during the discharging step.[4, 20]

Since we maintain a constant effluent concentration of 500 ppm and a productivity of 15 L m^{-2} h^{-1} across all feed salinities, a higher current density, and thus a higher average cell voltage, are required as the feed salinity is increased. Consequently, $\hat{E}_{fresh}$ increases with feed salinity, along with the ultimate cell voltage (i.e. the voltage at the end of charging period). It is important to note that as the cell voltage increases, so do the occurrence of Faradaic reactions (e.g. water electrolysis) which cause electrode degradation and significantly detract from the current efficiency of electrosorption.[30] Therefore, following previous theoretical and experimental studies, we constrain the cell voltage to a maximum of 1.6 V, limiting the treatable feed salinities for MCDI to the lower-end of the brackish water regime (<2300 ppm). Metzger et al., in contrast, seemingly do not consider a maximum cell voltage, as their MCDI curve extends far past our identified practical limit, into the seawater regime (up to ~40,000 ppm).

The MCDI curve shown in Figure 1 follows a similar trend to ED for low salinity feedwaters (i.e., <1 g L^{-1}), where the rate of growth in the specific energy consumption is large but steadies off as the brackish water region is approached. This is sensible since ED and MCDI — both being electro-driven technologies — incur a large potential drop from the high electrical resistance of dilute solutions. Once reaching the salinity of brackish waters, the energy consumption increases more linearly. We note that this linear trend is only valid for the lower end of the brackish water

197 regime we simulate, for which the effect of non-ideal co-ion leakage remains minimal. **Table 1.**
198 Specified parameters for the RO, ED, and MCDI modeling.

Technology	Parameter	Value
RO	Feed-side mass transfer coefficient (L m^{-2} h^{-1})	150
	Water permeability coefficient (L m^{-2} h^{-1} bar^{-1})	3
ED	Number of cell pairs,	50
	Spacer thickness (mm)	0.3
	Membrane thickness (mm)	0.13
	Membrane charge density (mol L^{-1})	3
	Bulk diffusion coefficient of NaCl in solution (m^2 s^{-1})	1.64×10^{-9}
	Effective diffusion coefficient of NaCl electromigration (m^2 s^{-1})	5.15×10^{-10}
	Diffusion coefficient of NaCl in the membrane (m^2 s^{-1})	1.64×10^{-10}
MCDI	Electrode macroporosity	0.43
	Electrode microporosity	0.4
	Stern layer capacitance (F mL^{-1})	120
	Specific external resistance (Ω cm^2)	30
	Specific electrode resistance (Ω mmol cm^{-1})	0.22
	Spacer thickness (mm)	0.26
	Electrode thickness (mm)	0.29
	Membrane thickness (mm)	0.15
	Membrane charge density (mol L^{-1})	3
	Bulk diffusion coefficient of NaCl in solution (m^2 s^{-1})	1.64×10^{-9}
	Diffusion coefficient of NaCl in the membrane (m^2 s^{-1})	1.64×10^{-10}

199

200 The energetic performance of RO and MCDI revealed in Figure 1 is notably different than that
201 of Metzger et al.'s Figure 6. Importantly, in Figure 1, we show that MCDI consumes more energy
202 than RO for most of the brackish water range, being competitive only for the desalting of very
203 dilute feeds (e.g. less than ~1000 ppm), for which energy consumption is very low (< 0.1 Wh/L)
204 and thus not a primary concern. In Figure 6 of Metzger et al., however, the energy consumption of
205 MCDI is shown to be lower than that of RO up to feed salinities above 15,000 ppm. Furthermore,

whereas Metzger et al. show that MCDI outperforms ED across the whole brackish water region, in Figure 1 we show the opposite trend, in which the energy consumption of ED is always lower than MCDI.

The effects of energy recovery in MCDI are also worth noting. Our results indicate that energy recovery in MCDI reduces $\hat{E}_{fresh}$, but not significantly enough to make it more energy efficient than RO or ED. Accordingly, we emphasize that the potential of energy recovery in CDI is limited, as only the energy stored in the electrical double layer is theoretically recoverable, with a large amount of energy irreversibly dissipating in other components of the MCDI cell (e.g. spacer channel and ion-exchange membranes).[20, 31] Though in our analysis we account for the practical energy losses in both the charging and discharging steps, it is important to note that even if no energy was lost in the discharging process — allowing for complete recovery of the energy in the electrical double layers — the energy consumption of MCDI would remain higher than RO and ED, as we have previously demonstrated.[19, 20]

As highlighted by the stark difference in our Figure 1 compared to Metzger et al.'s Figure 6, the authors' assessment of energy consumption is inadequate. Specifically, since the authors do not hold the separation parameters and productivity consistent across all technologies, the comparison of energy consumption is inherently flawed. Accordingly, the evaluation of the energetic capabilities of each of the assessed technologies in the study are misleading and should be reconsidered. In future technological comparisons of energy consumption, we emphasize the critical need to specify the separation parameters (i.e. feed salinity, extent of salt removal, and water recovery) and utilize more rigorous and mechanistic process modeling.

Conflicts of Interest

There are no conflicts to declare.

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