Supplemental Material: Thermodynamic limits of atmospheric water harvesting

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This supplement includes procedures that describe thermodynamic model derivations, processes diagrams (least work (S1), dew (S3), membrane (S11), and MOF/sorbent (S5)), supporting figures about recovery ratios (S2, S4, S12), model validation (S6), parametric sensitivity analyses (S8-S10), additional comparisons of processes with varying assumptions and efficiencies (S13-S15), and supporting temperature and humidity maps (S16-S18), as well as data.

- Document S1. Supplemental Procedures
- Figure S1. Least work process diagram
- Figure S2. Least work recovery ratio
- Figure S3. Ideal dew process diagram
- Figure S4. Maximum recovery in dew harvesting
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- Figure S6. Sorbent process model validation
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Additional References

Data S1. Dataset for all main text figures – spreadsheet attached separately
Supplemental Methods

Least work

The least work formulation begins with a steady-state balance of exergy for an irreversible open system.

\[
0 = \sum_0^in \dot{m} \hat{e} - \sum_0^out \dot{m} \hat{e} - W + Q \left(1 - \frac{T_0}{T}\right)
\]  

Where \(\hat{e}\) is the flow exergy, \(\dot{m}\) is the mass flow rate, \(W\) is the thermodynamic work and \(Q\) is the heat transfer. \(T_0\) represents the temperature of the thermodynamic dead state and \(T\) is the system boundary temperature. By grouping the path-dependent energy transfer terms in \(W_{\text{least}}\) we find that the least work is only a function of the ambient conditions.

\[
W_{\text{least}} = \sum_0^in \dot{m} \hat{e} - \sum_0^out \dot{m} \hat{e}
\]  

\[
\hat{e} = (h - h_0) - T_0(s - s_0)
\]

Where \(h_0\) and \(s_0\) are the enthalpy and entropy evaluated at the thermodynamic dead state. Expanding this form to include a conservation of mass, the least work is equivalent to the mass flow weighted sum of flow exergy. The equation is written on a basis of mass of water collected, which is equivalent to the change in absolute humidity of the ambient air. The infinitesimal change in bulk properties yields the theoretical minimum least work \(^1\).

\[
\dot{W}_{\text{least,min}} \frac{m_{\text{water}}}{\Delta \omega} = \lim_{\Delta \omega \to 0} \left( e_{\text{water}}(T) + e_{\text{HA}}(T) \frac{1 - \Delta \omega}{\Delta \omega} - e_{\text{HA}}(T) \frac{1}{\Delta \omega} \right)
\]

Where \(\omega\) represents the absolute humidity and \(\Delta \omega\) is the change in humidity of the ambient air. We define the maximum 2nd law efficiency as a function of the theoretical minimum least work and the work input from any given system, normalized by time or mass. The subscripts \(w\), \(HA\) represent water and humid air. The superscript * denotes that the property is evaluated at the concentration or humidity after recovery (\(\omega - d\omega\)).

\[
\eta_{II,\text{max}, i} = \frac{W_{\text{min, least}}}{W_i}
\]

Where \(\eta_{II,\text{max}, i}\) signifies the maximum second law efficiency of a given system and \(W_i\) is the work input required on a mass basis. \(i\) signifies a given process, such as dew, membrane, or MOF. This can be used as a generalized form to analyze all water harvesting systems on a consistent basis.

Dew harvesting

Extending this derivation, we model the energy consumption of an ideal dew collection process by assuming that a finite amount of water is separated from the bulk mixture and collected at the dewpoint temperature.

\[
\frac{W_{\text{dew}}}{m_{\text{water}}} = \dot{e}_{\text{water}}(T_{dp}) + \dot{e}_{\text{HA}}(T_{dp}) \frac{1 - \Delta \omega}{\Delta \omega} - \dot{e}_{\text{HA}}(T) \frac{1}{\Delta \omega}
\]

Here, \(T_{dp}\) is the dew point temperature. The flow exergy considers the ambient temperature as the thermodynamic dead state.

Metal-organic frameworks and sorbents

The sorbent system depends on the adsorption characteristics of the material. In order to provide a robust analysis, six MOFs and one polymeric sorbent with varying properties were considered to be representative and best performing for AWH applications among a review of hundreds of potential materials\(^2\). These MOFs/sorbents, and their key properties are shown below.
<table>
<thead>
<tr>
<th>MOF</th>
<th>RH_{desorb}</th>
<th>RH_{inflection}</th>
<th>W_{max} [kg/kg]</th>
<th>ΔH_{adsorb} [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-801</td>
<td>0.055</td>
<td>0.09</td>
<td>0.41</td>
<td>58.8</td>
</tr>
<tr>
<td>MOF-303</td>
<td>0.055</td>
<td>0.13</td>
<td>0.45</td>
<td>49</td>
</tr>
<tr>
<td>MIP-200(Zr)</td>
<td>0.16</td>
<td>0.18</td>
<td>0.45</td>
<td>55</td>
</tr>
<tr>
<td>Al-fumarate</td>
<td>0.16</td>
<td>0.27</td>
<td>0.45</td>
<td>50</td>
</tr>
<tr>
<td>Co_2Cl_4(BTDD)</td>
<td>0.2</td>
<td>0.29</td>
<td>0.87</td>
<td>45.8</td>
</tr>
<tr>
<td>MIL-101</td>
<td>0.2</td>
<td>0.4</td>
<td>1</td>
<td>50.85</td>
</tr>
<tr>
<td>Polymer</td>
<td>0.2</td>
<td>0.6</td>
<td>6.7</td>
<td>51.7*</td>
</tr>
</tbody>
</table>

*The enthalpy of adsorption for the hybrid polymer sorbent used was not available in the literature. After reviewing typical values for other polymers, the average $ΔH_{adsorb}$ of all MOFs reported in an exhaustive review paper was employed for the polymer. In effect, this neither favors nor diminishes the polymer material relative to the MOF materials, while still preserving the performance benefits associated with the polymer’s $RH_{desorb}$, $RH_{inflection}$, and $W_{max}$ properties.

$RH_{desorb}$ is the relative humidity needed to induce desorption, $W_{max}$ is the maximum water uptake for the MOF/sorbent, and $ΔH_{adsorb}$ is the enthalpy of adsorption for that adsorbent material. $RH_{inflection}$ is the relative humidity “inflection point” at which the water uptake is 50% of $W_{max}$. All this information is taken from prior work². Given the added complexity of considering numerous MOFs/sorbents, our modeling framework assumes a stepwise increase in water uptake from near-zero to $W_{max}$ at $RH_{inflection}$. This assumption is in line with the discussions of prior work² and enables easy modification of the model for new materials so other researchers can make use of the model. It also presents an idealized scenario for the sorbents.

There are several mass terms needed to evaluate the thermodynamics of the system, however, we would like to generalize the analysis by having everything in terms of the mass of water ultimately collected, $m_{water}$. Thus, the sorbent, adsorbed water, desorbed water, and desorption air masses are all defined per kilogram of collected water:

$$\frac{m_{ad}}{m_{water}} = \frac{w_{ad}}{(w_{ad} - w_{des})} \left(\frac{\omega_{cs} - \omega_{air}}{\omega_{cs} - \omega_{cond}}\right)$$  \hspace{1cm} (7)

$$\frac{m_{des}}{m_{water}} = \frac{\omega_{cs} - \omega_{air}}{\omega_{cs} - \omega_{cond}}$$  \hspace{1cm} (8)

$$\frac{m_{air}}{m_{water}} = \frac{1}{\omega_{cs} - \omega_{cond}}$$  \hspace{1cm} (9)

$$\frac{m_{MOF}}{m_{water}} = \frac{1}{w_{ad} - w_{des}} \frac{\omega_{cs} - \omega_{air}}{\omega_{cs} - \omega_{cond}}$$  \hspace{1cm} (10)

$m_{ad}$ and $m_{des}$ represent the mass of water that is adsorbed and desorbed in a cycle. $w_{ad}$ and $w_{des}$ are the water uptake values for the adsorption and desorption conditions, respectively. The subscript $cs$ signifies the air after water is desorbed into it. The subscript $cond$ represents the state of the condenser outlet. To evaluate the outlet humidity from the desorption, the integral average method was employed, as has been done in other modeling works⁴.

$$T_{a,i} = Temperature(\omega_{amb}, R_{des})$$  \hspace{1cm} (11)
\[ \omega_{cs} = \omega_{des, outlet} = \frac{T_{a,i} \int_{T_{airs}}^{T_{des}} \omega(RH_{des}T) dT}{T_{des} - T_{a,i}} \] (12)

Here, \( T_{a,i} \) is an “intermediate temperature” at which the relative humidity of the heated air is equal to the desorption relative humidity condition for the sorbent. \( T_{des} \) is the high temperature used for desorption. To determine the humidity at the outlet of the desorption process, the humidity ratio is integrated along the line of constant relative humidity and then divided by the total temperature difference, giving somewhat of an “average” outlet humidity condition. This can be further understood by the generic psychrometric chart below. Ultimately, the humidity ratio of the air leaving the desorption process is dependent on many process-specific parameters like flowrate, desorption rate, mass transfer coefficients and more. This integral method provides a straightforward way of calculating a reasonable “average” outlet condition. This method of determining the average outlet condition was introduced in prior work from another research group \(^4\).

Next, we define a recovery ratio for the process. In this case, we have defined the recovery ratio as the ratio of mass of humidity collected to the total mass of the humidity in the desorption air stream. Essentially, this gives the relative amount of water collected compared to the total amount of water vapor in the air entering the condenser.

\[ R = \frac{\omega_{cs} - \omega_{cond}}{\omega_{cs}} \] (13)

Here, everything is known except \( \omega_{cond} \). Thus, the recovery ratio controls the setpoint for the humidity of the air leaving the condenser, which controls the temperature of the condenser according to:

\[ T_{cond} = T_{sat}(\omega_{cond}, P_{atm}) \] (14)

Further, the recovery ratio not only controls the amount of water collected, but also the condenser temperature and the condenser performance since the condenser COP is tied to the condenser temperature.

The heat required to desorb the water vapor is described accordingly:

\[ \frac{Q_{des}}{m_{water}} = \left( \frac{m_{MOF}}{m_{water}} c_{p,MOF} + \frac{m_{ad}}{m_{water}} c_{p,w} + \frac{m_{air}}{m_{water}} c_{p,air} \right) (T_{des} - T_{air}) + \frac{m_{des}}{m_{water}} \Delta H_{ad} / MW_w \] (15)
The heat required to cool the desorption air and water vapor in the condensation process is calculated:

\[
\frac{Q_{\text{cond}}}{m_{\text{water}}} = h_g + c_p,v(T_{\text{des}} - T_{\text{sat}}(\omega = \omega_c)) + \frac{m_{\text{air}}}{m_{\text{water}}} (c_{p,\text{air}} + \omega_{\text{cond}}c_{p,v})(T_{\text{des}} - T_{\text{cond}})
\]  

(16)

Lastly, additional heat must be removed to return the MOF back to ambient conditions, which can be calculated as:

\[
\frac{Q_{\text{regen}}}{m_{\text{water}}} = \frac{m_{\text{MOF}}}{m_{\text{water}}} c_{p,\text{MOF}}(T_{\text{des}} - T_{\text{air}})
\]  

(17)

We can define ideal Carnot COP’s for cooling and heating according:

\[
COP_c = \frac{T_{\text{cond}}}{T_{\text{air}} - T_{\text{cond}}}
\]

(18)

\[
COP_h = \frac{T_{\text{des}}}{T_{\text{des}} - T_{\text{air}}}
\]

(19)

Thus, the ideal work input per kilogram of collected water is calculated as:

\[
\frac{W_{\text{MOF, min}}}{m_{\text{water}}} = \frac{q_{\text{des}}}{COP_h} + \frac{q_{\text{cond}} + q_{\text{regen}}}{COP_c}
\]

(20)

Cₚ values for different MOF’s/sorbents weren’t readily available in the literature, so to simplify the analysis, a Cₚ of 1 kJ/kg-K was used as the baseline (being very similar to that of MOF-801, Cₚ =1.14)¹. The sensitivity to this assumption is covered in this material.

Membranes

The open membrane system was assumed to have constant membrane parameters: 5000 GPU permeability to water vapor and 0 GPU permeability to N₂ and O₂. For consistency, the membrane area was taken to be 1 m² since the water flux scales linearly with area when concentration polarization is not considered. The flux through the membrane is defined by a force balance of water vapor at the membrane surface.

\[
\dot{m}_{\text{vapor}} = BA_m(p_v - p_{\text{sys}})
\]

(21)

Where \(\dot{m}_{\text{vapor}}\) is the vapor flowrate into the system, \(B\) is the membrane permeability to water vapor, and \(A_m\) is the membrane area, \(p\) is the partial pressure of water vapor and subscripts \(v\) and \(3\) signify the ambient vapor and the internal system. The membrane system model in this work was based off of the process proposed by Claridge et al. (2019) whereby the water vapor pulled across the membrane is compressed close to the saturation pressure at the ambient temperature by a separate water vapor compressor. A vacuum pump is also included to keep the whole system near-vacuum and to expel non-condensed gases back to the environment. Including this intermediate compression stage requires less sub-cooling to induce condensation. The pressure of this intermediate condensation stage \(p_{\text{ICS}}\) was chosen as 95% of the saturation pressure of water for the given ambient temperature:

\[
p_{\text{ICS}} = 0.95 \times p_{\text{sat}}(\text{water, } T_{\text{amb}})
\]

(22)

The heat required for condensation is found by an energy balance across the condenser according to the following equation:

\[
\frac{Q}{\dot{m}_{\text{vapor}}} = h_{\text{in}}(T_{\text{amb}}, p_{\text{ICS}}) - h_{\text{out}}(T_{\text{sat}}, x)
\]

(23)

Where \(h\) is the enthalpy of water vapor and subscripts \(\text{in}\) and \(\text{out}\) represent the inlet and outlet of the condenser, \(T\) is the temperature. Subscript \(\text{amb}\) represents ambient air and \(\text{sat}\) represents the saturation temperature at the system pressure. \(x\) is the desired quality exiting the condenser. Conversely this is related to the fractional recovery where \(x = 1\) signifies no condensation.
and $x = 0$ means that all incoming vapor is converted to liquid. The power consumption of the vacuum pump and compressor can be calculated according to the following equations.

$$W_{vac} = \dot{v}_{vapor} x(p_{amb} - p_{ICS})$$  \hspace{1cm} (24)

$$W_{comp} = \dot{v}_{vapor}(p_{ICS} - p_{sys})$$  \hspace{1cm} (25)

$$\dot{m}_{cond} = \dot{m}_{vapor}(1 - x)$$  \hspace{1cm} (26)

Where $W_{vac}$ is the vacuum pump energy, $W_{comp}$ is the compressor energy, and $\dot{v}$ is the volumetric flowrate of saturated water vapor at the saturation temperature. $\dot{m}_{cond}$ represents the amount of water vapor that is condensed and collected. The term $(1 - x)$ subtracts the amount of water vapor that is condensed. As described above, the heat to work conversion was delivered by a Carnot cooling device, operating between the saturation temperature of the system water vapor and the ambient temperature. The SEC, or specific energy consumption, is the sum of energy contributions divided by the amount of water collected.

$$W_{membrane} = \left( \frac{Q}{COP_c} + W_{vac} + W_{comp} \right)$$  \hspace{1cm} (27)
S1. Least work process diagram

a. Process schematic describing ambient air (1) flow being dehumidified (2) through an ideal atmospheric water device. The definition of the thermodynamic minimum represents a steady state, isothermal process. The thickness of each arrow qualitatively represents the relative magnitude of the mass flow rate. The color of each arrow represents the amount of water in the given stream, with more saturated colors signifying more water. The graph qualitatively describes the temperature (vertical axis) along the ideal process (horizontal axis).

b. The thermodynamic state of the air stream is described on the psychometric chart. Beginning at high humidity, and isothermally moving to low humidity. The change in absolute humidity between states 1 and 2 corresponds to the mass of water collected.
The least work trends are similar to those shown in previous analyses\textsuperscript{15}. This validates the inclusion of the limit as recovery goes to zero for the minimum least work, shown by Eq. 4. This trend varies significantly by the relative humidity.
S3. Ideal dew process diagram

a. The process schematic describes an ideal dew water harvesting device. Ambient air enters at the ambient temperature (1), is cooled to the dew point for condensation (2) (by a Carnot-like device), and then exits at a saturated state at the condenser temperature (3). The graph qualitatively describes the temperature of the air (vertical axis) along the dew harvesting process (horizontal axis).

b. The dew process for the humid air stream is visualized on the psychometric chart. The difference in humidity between (1) and (3) represents the mass of water collected.
S4. Maximum recovery in dew harvesting

The figure shows the recovery associated with subcooling a humid air mixture to the frost accumulation temperature. The lower bound of condenser temperature is limited by frost accumulation, and here is set to 273.15K. Lower condenser temperatures, or larger subcooling, induces higher recoveries and yields. In the case of a constant COP with respect to temperature, maximizing the recovery also maximizes the process efficiency. However, as shown by Fig 2 in the main text, when the COP is inversely proportional to the temperature difference, as is the case with a Carnot-device and many practical cooling systems, there is a trade-off between maximizing yield and efficiency.
S5. Ideal MOF/sorbent process diagram

The MOF/sorbent process aims to concentrate water vapor within a structure in cycles, to increase the humidity for more efficient condensation. The psychrometric chart represents the humid air states in the process after adsorption has occurred. Ambient air (1) is heated to a low relative humidity (2) where it can desorb the water contained within the MOF/sorbent. To facilitate desorption, the MOF/sorbent must be heated to a pre-defined relative humidity. The humidified air (3) is then sent to a condenser to extract water similar to the dew harvesting process. The graph qualitatively describes the temperature (vertical axis) along the desorption and condensation process (horizontal axis). The graph does not show the psychrometric process for the adsorption, which would simply be a dehumidification process since this is an open system.

The humid air states of the MOF/sorbent process are described on the psychometric chart. The process begins at an arbitrary inlet ambient air temperature and humidity. The collected mass of liquid water corresponds to the difference in humidity between (4) and (5).
S6. MOF/sorbent process model validation

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Kim et al. (2020)</th>
<th>This Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>System Type</td>
<td>Closed System (with internal recirculation)</td>
<td>Open System</td>
</tr>
<tr>
<td>Condensation</td>
<td>Occurs at ambient temperature, not accounted for in second law efficiency</td>
<td>Occurs at a specific condenser temperature, set according to an optimal recovery ratio, provided by a Carnot heat pump</td>
</tr>
</tbody>
</table>
| Desorption Process | Determines a minimum temperature, exceeds the minimum temperature, uses integral method to determine desorption outlet humidity ratio. | Uses similar methodology and assumptions, except that air fed to desorption process is ambient air, not recirculated air. RH of desorption is set at 5.5\%.

In order to provide confidence that our MOF/sorbent models were based on sound and established assumptions, we first replicated the closed-system modeling results from this prior literature, and then extended our open-system modeling framework having established good agreement between the closed-system models for a single material. Both models can take a known absolute humidity of the incoming air stream and determine the temperature for which that absolute humidity is 10\% relative humidity. The calculation for the minimum desorption temperature is the same between both models. In this work, ambient air is heated to attain the desorption relative humidity, whereas Kim et al. (2020) uses a saturated air stream at 25°C from the recirculation process. By setting the ambient condition to 25°C and 100\% RH in our model, we confirmed that our model would calculate a desorption temperature of 71°C, which is the minimum temperature determined by Kim et al. (2020). While this is only a small portion of the models, it is nonetheless a shared calculation between the two models which were matched. Attaining such desorption temperatures could be provided by various heat pump technologies, solar heating, electric heating, and more. However, in this work we explicitly model the process as having all heating and cooling provided by a Carnot device, remaining system-design agnostic.

Furthermore, the cycle model for the single-cycle recirculation system presented by Kim et al. (2020) was replicated for MOF-801, and the thermal efficiency compared nicely. The foundational assumptions about operating conditions for both models match and can reproduce results of the prior published work.

![Thermal Efficiency Graph](image1)

The open system was chosen as it is the simpler option that is more robust and flexible to adapt to different MOFs/sorbents and operating conditions. Additionally, it is the most comparable system to the other AWH systems modeled in this work (dew, membrane, and least work). So, while the two systems are different in several aspects, they also share many similarities as discussed above. The framework developed in this work is developed with a very similar approach.
S7. MOF/Sorbent characteristic isotherms

<table>
<thead>
<tr>
<th></th>
<th>RH&lt;sub&gt;desorb&lt;/sub&gt;</th>
<th>RH&lt;sub&gt;infection&lt;/sub&gt;</th>
<th>W&lt;sub&gt;max&lt;/sub&gt; [kg/kg]</th>
<th>ΔH&lt;sub&gt;adsorb&lt;/sub&gt; [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-801</td>
<td>0.055</td>
<td>0.09</td>
<td>0.41</td>
<td>58.8</td>
</tr>
<tr>
<td>MOF-303</td>
<td>0.055</td>
<td>0.13</td>
<td>0.45</td>
<td>49</td>
</tr>
<tr>
<td>MIP-200(Zr)</td>
<td>0.16</td>
<td>0.18</td>
<td>0.45</td>
<td>55</td>
</tr>
<tr>
<td>Al-fumarate</td>
<td>0.16</td>
<td>0.27</td>
<td>0.45</td>
<td>50</td>
</tr>
<tr>
<td>Co&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;(BTDD)</td>
<td>0.2</td>
<td>0.29</td>
<td>0.87</td>
<td>45.8</td>
</tr>
<tr>
<td>MIL-101</td>
<td>0.2</td>
<td>0.4</td>
<td>1</td>
<td>50.85</td>
</tr>
<tr>
<td>Polymer</td>
<td>0.2</td>
<td>0.6</td>
<td>6.7</td>
<td>51.7*</td>
</tr>
</tbody>
</table>

In this work, seven materials with ranging adsorption properties were implemented. In order to simplify the analysis, given the broad scope of this work, each material was assumed to experience a stepwise increase in water vapor uptake at RH<sub>infection</sub>. In other words, for any ambient relative humidity greater than RH<sub>infection</sub>, the MOF/sorbent experiences the tabulated maximum uptake. This assumption has been used in other broad works<sup>3</sup> and represents the behavior of an idealized MOF isotherm. By implementing seven different sorbents, the model can decide which MOF properties to use based on the ambient relative humidity. The breakdown of when each MOF is used is summarized as follows:

\[
\begin{align*}
RH & \leq 0.13 & \Rightarrow \text{use MOF-801 properties} \\
0.13 & \leq RH < 0.18 & \Rightarrow \text{use MOF-303 properties} \\
0.18 & \leq RH < 0.27 & \Rightarrow \text{use MIP-200(Zr) properties} \\
0.27 & \leq RH < 0.29 & \Rightarrow \text{use Al-fumarate properties} \\
0.29 & \leq RH < 0.40 & \Rightarrow \text{use Co}<sub>2</sub>Cl<sub>2</sub>(BTDD) properties \\
0.40 & \leq RH < 0.60 & \Rightarrow \text{use MIL-101 properties} \\
RH & \geq 0.60 & \Rightarrow \text{use polymer properties}
\end{align*}
\]
Here, a sensitivity analysis of recovery ratio, defined earlier in this supplementary information, is conducted. Specifically, the specific energy consumption for the water harvesting cycle and condenser temperature are evaluated. To achieve higher recoveries, the condenser temperature must be set lower since the recovery is related to the difference between the dew point temperature and the condenser temperature. Each plot was evaluated for an ambient air temperature of 300K or 310K.

The adsorbent system clearly displays a dependence on the recovery ratio. At low recovery ratios, warmer condenser temperatures can be used, which leads to a higher cooling COP. However, this is offset by the low amount of water collected, leading to higher specific energy consumption. At high recovery ratios, the opposite is true. Lower temperatures are used to achieve higher recovery, which leads to lower cooling COP in conjunction with the increased water collection. The next effect is high specific energy consumption.

The optimal recovery under these conditions is usually on the order of 70-80%. However, it can also be seen that a recovery of 80% requires sub-freezing condenser temperatures for low ambient humidity conditions. For this reason, a recovery ratio of 65% was set in order to ensure that sub-freezing condenser temperatures are avoided under most conditions. Additionally, setting the recovery ratio at 65% leads to a marginal difference in performance. For example, for the 310K scenario, the specific energy consumption at 65% recovery is only 3.5% higher than the true optimal conditions. Thus 65% recovery is near-optimal and avoids sub-freezing conditions.
A sensitivity analysis was conducted with assumed parameters in the adsorbent model, to show the relative effects on the energy consumption. The default analysis conditions include the ambient relative humidity of 50%, the specific heat capacity (1 kJ/kg K), and recovery ratio of 0.65, and sorbent-specific properties in presented previously. As can be seen, the specific heat capacity, adsorption energy, and maximum water uptake of the MOF have very minimal impact on the specific energy consumption. However, these variables may significantly impact the non-normalized energy consumption, which may be important in practical systems with size and form factor constraints.

The most significant factor affecting the specific energy consumption for water harvesting is the desorption relative humidity. Due to the integral method used to determine the outlet humidity ratio from the desorption process, even small increases in the desorption relative humidity led to significant increases in the outlet humidity ratio. Thus, for a constant recovery ratio, a significant increase in desorption outlet humidity ratio leads to a higher condenser temperature and cooling COP, greatly improving the specific energy consumption of the system. However, at sufficiently high values of RH_{des}, increasing this value provides diminishing returns, shown in the following figure. Essentially, while the specific energy consumption for desorption and condensation decrease, they level out at a non-zero minimum. More water is collected, and therefore the denominator of the specific energy consumption for desorption increases, but the absolute amount of energy required to desorb that humidity also increases (numerator), explaining this tradeoff.
S10. MOF/sorbent desorption humidity

We further demonstrate the strong dependence on desorption RH in the plots above. These plots show the specific energy consumption of water harvesting at an ambient temperature of 300K with varying ambient relative humidity (x-axis). The left plot employs the MOF assumptions from Section S7 exactly, showing the region in which each MOF/sorbent operates. Whereas the right plot employs a constant desorption relative humidity (5.5% RH) but lets all other MOF/sorbent properties switch based on the ambient relative humidity. It can be seen that when all MOFs/sorbents use the same desorption relative humidity, the energy consumption across the range of humidity values (still switching between all 7 materials) essentially collapses to a single curve, with some jagged points where material properties switch. In the main text, we use all 7 MOFs/sorbents while employing a their “true” desorption relative humidity values from prior literature as described in Section S7.
S11. Ideal membrane process diagram

**Diagram a.** The membrane process employs a membrane to isothermally concentrate water vapor before condensation. This is a depiction of the original Claridge-Culp-Liu dehumidification process. The psychrometric chart represents the humid air states in the process. Ambient air (1) is concentrated (2) where now it has a lower energy requirement for condensation. The water vapor is condensed and then is pumped back to atmospheric pressure. Note: only the air states are shown in the psychrometric chart. Since the membrane is assumed to be perfectly selective, only water vapor enters the condenser.

**Diagram b.** The humid air states of the membrane process are described on the psychrometric chart. The process begins at an arbitrary inlet ambient air temperature and humidity. The collected mass of liquid water corresponds to the difference in absolute humidity between 1 and 2 minus the amount of excess vapor that is rejected from the system.
The breakeven recovery represents the recovery ratio at which the membrane must operate to be energy-equivalent to dew harvesting. In the membrane system, it is always optimal to condense all the water vapor that passes through the membrane. In the case that this happens, the membrane system will require less energy than dew. However, achieving high recovery through heat exchangers may have practical limitations such as scaling and frost.
The breakeven efficiency refers to the isentropic efficiency of the vacuum pump in the membrane system that allows the membrane to be energy-equivalent to the dew harvesting process. The figure on the left assumes a compressor efficiency of 50%, while the figure on the right sets the compressor efficiency to 90%. The sub-saturated region in white represents the area where dew is better than the membrane even with isentropic vacuum pumping. This white region becomes larger with lower compressor efficiency and lower recovery. The default recovery for the membrane system is 65%, which was chosen to create a fair comparison on the basis of yield with the MOF-sorbent process.
Dew harvesting, membrane, and sorbent processes are modeled with cooling and heating coefficient of performances of 3 and pump isentropic efficiencies of 65% (compressor) and 20% (vacuum pump). This represents a first order estimate of current heating and cooling technologies, although in practice larger temperature differences will yield lower efficiency components and technologies for near-saturation pumping may encounter additional issues. The contour axis is represented on a log scale in units of kJ/kg.
The air temperature at 2m above the surface is mapped, based on the monthly NASA MERRA2 database. The spatial resolution of data was 0.5° in latitude and 0.625° in longitude. The median (a) and standard deviation (b) are taken from monthly mean temperatures (January 2019 to January 2021). The mapping approach considered each time-step individually.
S16. Global humidity map and standard deviation

The specific humidity at 2m above the surface is mapped, based on the monthly NASA MERRA2 database\(^6\). The spatial resolution of data was 0.5° in latitude and 0.625° in longitude. The median (a) and standard deviation (b) are taken from monthly mean temperatures (January 2019 to January 2021). The mapping approach considered each time-step individually.
S17. Months of the year with mean temperature above 274K

The number of months in a year where the surface temperature is above 274K is mapped, based on the monthly NASA MERRA2 database. The spatial resolution of data was 0.5° in latitude and 0.625° in longitude. The median (a) and standard deviation (b) are taken from monthly mean temperatures (January 2019 to January 2021). The mapping approach considered each time-step individually.
**Additional references**


**Data S1. Dataset for all main text figures**

The data set is in a spreadsheet file formatted like a data frame format and represents the information used to create Fig. 1a. Columns have information on temperature, humidity, least work, optimal recovery ratio for dew harvesting, and ideal energy requirements for: dew harvesting, membrane systems, and sorbent systems. Optimal recovery is defined as the recovery ratio that requires the minimum energy requirement. It is found by finding the minimum of the function shown in Fig. 2a. The ranges for temperature and humidity match those commonly found most environments on Earth. The energetics of harvesting vapor from extreme cold and extreme heat require further study.