Contribution of surface energy to pH dependent underwater adhesion of an acrylic pressure sensitive adhesive

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The Supporting Information contains 16 Pages with 8 Figures, and 7 Tables.
1 Probe tack measurements

1.1 Schematic and typical debonding force curve

Figure S1. (a) Schematic of probe-tack apparatus. Roberts et al.\(^1\) provides a very detailed description of the experimental apparatus. (b) Illustration of OTS glass probe and 5\%AA surface chemistry in air. (c) Typical force-time curve for probe tack of PSA in pH solution. PSA is immersed in pH solution for 10 minutes, while the hydrophobic probe is in air. The cantilever is lowered at a velocity of 50 \(\mu\)m/s (approach) until it applies a 10mN compressive normal force to the sample. Contact between the probe and PSA is thereby made in solution. The cantilever is held at -10 mN using a force feedback loop for a dwell time of 100s. Subsequently the cantilever is retracted at 50 \(\mu\)m/s. Compressive forces are negative.
1.2 System compliance

The slope of the probe tack curve depends on the compliance of the system (PSA and instrument). The compliance of the system can be calculated from

\[ C_{\text{System}} = C_{\text{PSA}} + C_{\text{Cantilever}} \]  

(S1)

\[ C_{\text{PSA}} = \frac{C_o}{1 + \frac{0.75}{2.8(1-2\nu)} \left( \frac{a}{h} + \left( \frac{a}{h} \right)^3 \right)} \]  

(S2)

Where \( C_o = \frac{3}{8Ea} \), \( a \) is the radius of contact, \( h \) is the thickness of PSA, \( \nu \) is the poisson ratio of the PSA, \( E \) is the elastic modulus of the PSA. \( E \) can be approximated as 3G for \( \nu=0.5 \), where G is obtained from rheological measurements. \( C_{\text{Cantilever}} \) can be obtained from the spring constant of the cantilever and is 2.22x10^{-4} m/N. Table S1 shows the stiffness (Compliance^{-1}) for both PSAs. The standard deviation for calculated values is obtained using error propagation from rheology.

Table S1. Comparison between the compliance obtained from the force-detachment curve and the compliance calculated based on materials properties for 5%AA and 0%AA PSAs in different environments. In (I) \( 1/C_{\text{System}} \) is calculated using equation S1 and S2. In equation S2 the compliance of the PSA is evaluated using the moduli from oscillatory rheology. In (II) \( 1/C_{\text{System}} \) is obtained directly from initial slope of probe tack curve (linear regime) during detachment.

| PSA  | Environment | \( C_{\text{PSA}} \) (m/N) | \( C_{\text{System}} \) (m/N) | \( 1/C_{\text{System}} \) (N/m) | \( 1/C_{\text{System}} \) (N/m) |
|------|-------------|-----------------------------|--------------------------------|-------------------------------|-------------------------------|
|      |             |                             | I                             | II                                           |                                |
| 5%AA | Air         | 6.70 x10^{-5}              | 2.89 x10^{-4}              | 3457 ± 609                      | 3814 ± 574                      |
|      | pH 3        | 7.18 x10^{-5}              | 2.94 x10^{-4}              | 3401 ± 709                      | 3742 ± 696                      |
|      | pH 11       | 8.97 x10^{-5}              | 3.12 x10^{-4}              | 3206 ± 508                      | 3570 ± 583                      |
| 0%AA | Air         | 5.44 x10^{-5}              | 2.77 x10^{-4}              | 3615 ± 544                      | 3195 ± 485                      |
|      | pH 3        | 4.81 x10^{-5}              | 2.70 x10^{-4}              | 3699 ± 436                      | 3316 ± 378                      |
|      | pH 11       | 4.83 x10^{-5}              | 2.71 x10^{-4}              | 3697 ± 653                      | 3301 ± 602                      |
Thus, some variation in the slope can be expected from the standard deviation in rheology of PSA. The variation in slopes in Figure 1, Figure 2 falls within the standard deviation of calculated values.

2 Contact angle measurements

2.1 Contact angle titration

To determine the pK\textsubscript{a} of 5\%AA PSA we follow the approach of Bain\textsuperscript{3}. We consider the PSA surface as a composite surface consisting of surfaces with protonated and deprotonated carboxyl group separately. According to Cassie’s law\textsuperscript{4}, the contact angle of different pH buffer solution on this composite surface is expressed by:

\[
\cos \theta_{13} = \alpha_{RCOO^{-}} \cos \theta_{RCOO^{-}} + \alpha_{RCOOH} \cos \theta_{RCOOH}
\]  
(S3)

where \( \theta_{13} \) is apparent contact angle of pH buffer solution (3) on 5\%AA PSA surface (1), \( \alpha_{RCOO^{-}} \) and \( \alpha_{RCOOH} \) are pH dependent area fractions of deprotonated and protonated PSA surface respectively. \( \theta_{RCOO^{-}} \) and \( \theta_{RCOOH} \) are the contact angles of water on completely deprotonated PSA surface and completely protonated PSA surface respectively \( \theta_{RCOO} \) and \( \theta_{RCOOH} \) are measured by using extreme high (pH11) or low pH (pH3) solution as drop liquid. Since carboxyl group is distributed uniformly on the PSA surface, the area fractions \( \alpha_{RCOO^{-}} \) and \( \alpha_{RCOOH} \) are equivalent to molar fractions of deprotonated and protonated carboxyl group and can be written as:

\[
\alpha_{RCOO} = \frac{[RCOO^{-}]}{[RCOO^{-}] + [RCOOH]}; \quad \alpha_{RCOOH} = \frac{[RCOOH]}{[RCOOH] + [RCOO^{-}]} 
\]  
(S4)

Thus, for binary composite surface, obviously we have \( \alpha_{RCOO^{-}} + \alpha_{RCOOH} = 1 \), where \( \alpha_{RCOO^{-}} \) is also called dissociation ratio and equation S3 becomes:

\[
\alpha_{RCOO} = \frac{\cos \theta_{13} - \cos \theta_{RCOOH}}{\cos \theta_{RCOO} - \cos \theta_{RCOOH}} 
\]  
(S5)

For monoprotic acid, the definition of dissociation constant \( K_{\text{a}} \) is:

\[
K_{\text{a}} = \frac{[RCOO^{-}][H^{+}]}{[RCOOH]} 
\]  
(S6)

Combine equation S4 and S6:
\[
\alpha_{\text{RCOO}} = \frac{10^{pH-pK}}{1+10^{pH-pK}}
\] (S7)

In S5, since \( \theta_{\text{13}}, \theta_{\text{RCOO}} \) and \( \theta_{\text{RCOOH}} \) are all measurable, the dissociation ratio of carboxyl group in our PSA sample at different pH is easy to be determined. Thus, by plotting pH verses dissociation ratio and performing regression, we can obtain the pK\(_a\) of carboxyl group on the surface.

2.2 Determination of the surface energy of the PSAs
Calculating surface energy from contact angle measurement is a widely used method\(^5-6\). It is based on Young’s equation, where an equilibrium multi-phases system (vapor-solid-liquid) is assumed. The contact angle is determined by:

\[
\gamma_3 \cos \theta_{\text{13}} = \gamma_1 - \gamma_{13}
\] (S8)

where \( \gamma_1 \) is the surface energy of PSA in air, \( \gamma_3 \) is the interfacial tension of pH solution in air, \( \gamma_{13} \) is the surface energy of PSA in water and \( \theta_{\text{13}} \) is the contact angle of pH solution drop on PSA surface in air. The equilibrium film pressure of adsorbed vapor on the solid surface (\( \pi_e \)), is generally small and has been neglected\(^5\). In equation (S8), \( \gamma_3 \) and the contact angle \( \theta_{\text{13}} \) is measured from contact angle and pendant drop measurements, while \( \gamma_{13} \) and \( \gamma_1 \) (two unknowns) are not directly measurable from a single contact angle measurement. Several theories successively evolved based on the same idea of partition of surface energy into individual components\(^5-7\). Owens’ equation\(^5\) is one of the most frequently used:

\[
\gamma_1 = \gamma_1^d + \gamma_1^p
\] (S9)

\[
\gamma_{13} = \gamma_1 + \gamma_3 - 2\sqrt{\gamma_1^d \gamma_3^d} - 2\sqrt{\gamma_1^p \gamma_3^p}
\] (S10)

Combining equation S8, S9 and S10, we get:

\[
\frac{\cos \theta_{\text{13}} + 1}{2} \gamma_3 = \sqrt{\gamma_1^d \gamma_3^d} + \sqrt{\gamma_1^p \gamma_3^p}
\] (S11)

To solve this system of equations with two unknows, two liquids including one polar and one apolar should be chosen to reduce numerical error. Here, we chose water and diiodomethane as our liquids to measure surface energy of PSA in air. To measure surface energy of PSA in pH solution, we chose pH buffer solution drop (fluid A) and diidomethane (fluid B). Based on advancing angles we obtain \( \gamma_1 = 7 \pm 2 \text{ mJ/m}^2 \) for 5\%AA and \( 8 \pm 2 \text{ mJ/m}^2 \) for 0\%AA. Clearly the
values are unrealistically low because of surface roughness. The contact angles and surface energy values of both PSAs at different pH are shown in Table S2 and Table S3.

**Table S2.** Receding (Rec) and advancing (Adv) contact angle (θ) measurements with probe fluid A: pH buffer solution and probe fluid B: diiodomethane on 5%AA and 0%AA.

| pH | Fluid A pH drop | Fluid B Diiodomethane |
|----|----------------|-----------------------|
|    | θ_{Adv}^{13}   | θ_{Rec}^{13}          | θ_{Adv}^{13} | θ_{Rec}^{13} |
| 3  | 125 ± 2        | 62 ± 5                | 100 ± 6      | 30 ± 2       |
| 6  | 123 ± 1        | 62 ± 3                | 102 ± 5      | 32±2         |
| 8  | 126 ± 1        | 56 ± 6                | 112 ± 1      | 62 ± 1       |
| 11 | 124 ± 1        | 47 ± 1                | 112 ± 1      | 62 ± 1       |

**Table S3.** Surface energy in air and in water calculated from contact angle measurement. 3= water (pH buffer solution), Rec=calculated from receding angle, Adv= calculated from advancing angle, d= dispersion component, p= polar component.

| pH | Surface energy of PSA (mJ/m²) |
|----|-------------------------------|
|    | From receding contact angles  | From advancing contact angles |
|    | γ_{Rec,d} | γ_{Rec,p} | γ_{Adv} | γ_{Adv} |
| 3  | 32    | 14          | 7      | 7       |
| 6  | 32    | 15          | 7      | 7       |
| 8  | 31    | 19          | 7      | 7       |
| 11 | 27    | 27          | 7      | 7       |

3. *Calculation of work of adhesion from contact angle measurements*

The work of adhesion (W_{adh}) of 0%AA and 5%AA is calculated from the contact angle measurements using equation (S12)^8:
\[ W_{\text{ad}} = \gamma_{13} + \gamma_{23} - \gamma_{12} \; \gamma_{ij} = \left( \sqrt{\gamma_i} - \sqrt{\gamma_j} \right)^2 \]  

where the subscripts 1, 2 and 3 represent the PSA, OTS probe and pH medium respectively (as shown in Figure S2). \( \gamma_{ij} \) represents the interfacial energy between \( i \) and \( j \). \( \gamma_2 = 20 \text{ mJ/m}^2 \) is the surface energy of the OTS surface (probe) in air obtained from Zisman plots\(^9\). \( \gamma_1 \) is the surface energy of the PSA in air and is obtained from receding contact angle measurements using DI water and diiodomethane as probe liquids. \( \gamma_3 = 73 \pm 1 \text{ mJ/m}^2 \) is the surface tension of the pH solution.  
\( \gamma_{12} \) is the interfacial energy of the PSA-probe interface and is equal to 3 mJ/m\(^2\) for both PSAs (from equation 2). \( \gamma_{23} = 16 \text{ mJ/m}^2 \) is the surface energy of the OTS probe in pH solution (from equation 2). \( \gamma_{13} \) is the surface energy of the PSA-pH solution interface shown in Table S3. Table S4 provides values of work of adhesion for both PSAs in air and in pH solution.

![Figure S2](image.png)

**Figure S2.** Schematic to represent OTS glass probe bonded to PSA surface. The subscripts for surface energies are illustrated here as 1- PSA surface, 2-OTS probe surface, and 3-pH medium.

**Table S4.** Calculated value for the work of adhesion between PSA-probe in air and PSA-probe in solutions with different pH.

| PSA  | Medium | \( \gamma_{13} \) (mJ/m\(^2\)) | \( W_{132} \) (mJ/m\(^2\)) |
|------|--------|-------------------------------|-----------------------------|
| 5% AA| Air    | 45 ± 2                        | 64 ± 2                      |
|      | pH 3   | 13 ± 3                        | 28 ± 3                      |
|      | pH 6   | 12 ± 2                        | 27 ± 2                      |
|      | pH 8   | 9 ± 3                         | 24 ± 3                      |
|      | pH 11  | 4 ± 1                         | 19 ± 1                      |
| 0% AA| Air    | 46 ± 2                        | 65 ± 2                      |
|      | pH 3   | 14 ± 2                        | 27 ± 2                      |
|      | pH 6   | 11 ± 1                        | 24 ± 2                      |
|      | pH 8   | 12 ± 1                        | 25 ± 1                      |
|      | pH 11  | 11 ± 1                        | 24 ± 1                      |
4. Surface Zeta Potential measurements

![Figure S3](image)

**Figure S3.** Plot of apparent zeta potential of sulfated polystyrene latex particles vs. distance from the PSA surface for 5%AA in pH 10 solution. From the plot, the apparent zeta potential of the latex particle near the surface can be approximated as the intercept on the y-axis as $\zeta_{\text{tracer, apparent}} = 44.6$ mV. The true zeta potential of latex particles is calculated at a distance of 1000 $\mu$m which is far away from the surface as $\zeta_{\text{tracer, true}} = -40.5$ mV. The surface zeta potential can then be calculated as $\zeta_{\text{surface}} = \zeta_{\text{tracer, true}} - \zeta_{\text{tracer, apparent}} = 85.1$ mV. The same measurement is repeated thrice to get an average value of SZP.

5. Poisson Boltzmann equation

The forces between the PSA and the glass-probe surface can be treated as a sum of the electrostatic repulsion and the van der Waal attraction between the two surfaces. The electrostatic contribution to the interaction between the PSA and the probe can be simplified and modelled using the Poisson-Boltzmann equation for two uniformly charged plates with different surface potentials in a symmetric electrolyte in 1D:

$$\frac{d^2\Psi}{dx^2} = \frac{2\rho_e z e}{\varepsilon \varepsilon_0} \sinh \left( \frac{z e \Psi}{k_b T} \right)$$  \hspace{1cm} (S13)
Non-dimensionalizing equation S13 with $y = \frac{ze^\Psi}{k_BT}$ and $\xi = \kappa x$ where $\kappa = \left(\frac{2\rho_\infty z^2e^2}{k_BT\varepsilon_0\varepsilon_r}\right)^{1/2}$ is the inverse of the Debye length. $\rho_\infty$ is the concentration of ions far away from the surface, $z$ is the valency of the ion in the 1:1 electrolyte, $e$ is electronic charge, $k_B$ is the Boltzmann constant, $T$ is the temperature and $\varepsilon_0$ and $\varepsilon_r$ are the permittivity of free space and dielectric constant of water respectively, we then get:

$$\frac{d^2y}{d\xi^2} = \sinh(y)$$

(S14)

We approximate the PBS buffer solution as solution of NaCl to satisfy the condition for a 1:1 electrolyte. The Debye length $\kappa = \frac{0.304}{\sqrt{C}} = 6.8$ nm where $C = 2$ mM. We can obtain $\Psi(x)$ by solving equation S14 numerically in MATLAB and reintroducing the dimensional parameters. We assume a constant potential boundary condition where the surface potential at both surfaces is approximated by the SZPs of the PSA and OTS (See Table S5 below), where both depend on the pH of the solution.

**Table S5.** Surface zeta potential of 5%AA and OTS at different pH

| pH | Surface Zeta Potential (mV) |
|----|-----------------------------|
|    | 5% AA | OTS | 5% AA | OTS |
| 3  | -1 ± 32 | -15 ± 6 | 5% AA | OTS |
| 4  | -23 ± 4 | -39 ± 3 | 5% AA | OTS |
| 6  | -39 ± 20 | -36 ± 4 | 5% AA | OTS |
| 8  | -67 ± 55 | -40 ± 0 | 5% AA | OTS |
| 10 | -104 ± 16 | -56 ± 12 | 5% AA | OTS |
| 11 | -100 ± 7 | -52 ± 7 | 5% AA | OTS |

We obtain the pressure ($P$) between two charged flat plates using equation S15 and the interaction energy from equation S16.

$$P(D) = 2nk_BT \cosh \left( \frac{e^\Psi}{k_BT} \right) - 1 - \frac{\varepsilon_0\varepsilon_r}{2} \left( \frac{d^2\Psi}{dx^2} \right)^2$$

(S15)

$$W_\alpha(D) = -\int_{\infty}^{D} P(D)dD$$

(S16)
where $n$ is the concentration of the electrolyte, $D$ is the distance between the two plates. The interaction energy due to van der Waal’s interaction between two flat plates is given by:

$$W_{\text{vdW}} = -\frac{A_H}{12\pi D^2},$$  \hspace{1cm} (S17)

where $A_H = 3.44 \times 10^{21}$ J is the Hamaker constant for PSA-OTS in water, and obtained from combining relations$^8$. The total interaction energy $W_{\text{total}}$ can be written as:

$$W_{\text{total}} = W_{\text{vdW}} + W_{\text{el}}.$$  \hspace{1cm} (S18)

![Figure S4](image)

**Figure S4** Plot of the total interaction energy $W_{\text{total}} = W_{\text{vdW}} + W_{\text{el}}$ vs. separation between the PSA and OTS surface.

We calculate the total interaction energy and determine the maximum repulsive interaction (maxima in Figure S4). We obtain the maximum force from $F_{\text{sphere}} = 2\pi R W_{\text{flat}}$ for the sphere-plane geometry, relying on Derjaguin’s approximation$^8$, with $R = 7.06$ mm is the radius of the OTS probe. From this, we obtain $W_{\text{flat}} = 0.047$ mJ/m$^2$ and $F_{\text{max}} = 2$ $\mu$N for pH 4 and $W_{\text{flat}} = 0.337$ mJ/m$^2$ and $F_{\text{max}} = 15$ $\mu$N for pH 10. At pH3, we do not see a positive peak and the total interaction energy is purely attractive.
6. In-situ fingering wavelength analysis

We can also infer a change in the surface energy of the PSA-fluid interface from the fingering instability present during debonding using the analysis for a Saffman-Taylor instability.\textsuperscript{10} The analysis is based on a linear instability analysis reported by Nase \textit{et al.}\textsuperscript{11}, where the interfacial energy of the PSA, $\gamma$, can be obtained from the debonding process using

$$\gamma \propto (\lambda \sqrt{U})^2$$

where $\lambda$ is the wavelength of the fingers and $U$ is the radial velocity of the fingers during the debonding process (assuming constant viscosity).

Fingering image analysis is done by converting the images captured by the MFM camera into 8-bit black and white images in ImageJ (Figure S5). The following steps are followed to calculate the instantaneous radial velocity and wavelength of fingers:

1. An approximate center of each image is obtained by fitting the contact image to a circle manually and recording the coordinates and radii. A common center for all images is obtained by taking an average over all the x and y coordinates.

2. The instantaneous wavelength is obtained by counting the number of fingers $n$ and dividing the perimeter obtained from the fitting circles by $n$.

3. The distance of the finger approaching inwards towards the center is calculated for four to five different fingers spanning 360° for each image. The increment of distance $dx$ is obtained by calculating how much each finger moved between consecutive images. An instantaneous value of velocity is obtained by dividing $\Delta r$ by the time increment between images.

4. To obtain a single value of instantaneous radial velocity for each image, the value is averaged over all the fingers.
Figure S5. Example of fingering wavelength analysis in Image J. The five arrows represent the fingers with maximum growth in the radial direction. Dotted grey line represents the circle which is fit manually to obtain the perimeter $= n \lambda$ where $n$ is the number of fingers and $\lambda$ is the wavelength of the fingers.

The inflow of water and retraction of the PSA can be modelled as a Saffman-Taylor instability which is governed by the surface tension at the interface of two fluids of which the less viscous fluid flows into a more viscous fluid. The instabilities take the shape of fingers that protrude into the more viscous liquid. Using linear stability analysis\textsuperscript{11}, the relationship between the surface tension $\gamma$ and the maximum wavelength of instability $\lambda_{max}$ can be obtained as:

$$\lambda_{max} = \pi b \sqrt{\frac{\gamma}{U (\eta_1 - \eta_3)}}$$  \hspace{1cm} (S20)

Where $U$ is the radial velocity of fingering, $\eta_3$ is the viscosity of the penetrating fluid (water), $\eta_1$ is the viscosity of the retracting fluid (PSA) and $b$ is the distance between the two surfaces.

As $\eta_1 \ll \eta_3 = \eta$,

$$\lambda_{max} = \pi b \sqrt{\frac{\gamma}{U \eta}}$$  \hspace{1cm} (S21)

The given relationship can be rearranged (assuming the viscosities to be the same in air and pH solution) to get S19. It is worth noting that the quantities presented here are all instantaneous. To get an average surface energy as a function of pH, the time-dependent variables $\lambda$ and $U$ are
obtained as a function of time. The region in which the surface energy is calculated is the region of constant radial velocity (see Figure S6) for equation (S21) to be valid.

**Table S6.** Time from onset of fingering, radial velocity of fingers ($U$), wavelength of fingers ($\lambda$) and $\lambda\sqrt{U}$ for fingering images at pH 3 for 5%AA PSA.

| Time (ms) | $U$ (µm/s) | $\lambda$ (µm) | $\lambda\sqrt{U}$ (µm$^{1.5}$s$^{-0.5}$) |
|-----------|-------------|----------------|-----------------------------------------|
| 0.022     | 91          | 197            | 1879                                    |
| 0.055     | 74          | 194            | 1671                                    |
| 0.088     | 81          | 194            | 1748                                    |
| 0.122     | 88          | 191            | 1796                                    |
| 0.154     | 98          | 217            | 2141                                    |
| 0.186     | 199         | 212            | 2990                                    |
| 0.221     | 277         | 208            | 3465                                    |
| 0.253     | 744         | 200            | 5453                                    |

**Figure S6.** Plot of radial velocity vs. time from fingering images obtained for one set of data at pH = 3 (5%AA). The radial velocity is almost constant till 0.15 ms after which it increases exponentially. We therefore calculate the average surface energy at pH 3 over the values in this window. A final value of $(\lambda\sqrt{U})^2$ is obtained by repeating the same analysis at each pH thrice and taking an average over different samples.
Figure S7. Plot of $G_0 \tan \delta$ vs $G'b$ at different pH for 0%AA (open symbols) and 5% AA (closed symbols) PSA. $G_0$ is the threshold fracture energy obtained from work of debonding for each PSA. $G'$ is the storage modulus obtained from frequency sweep rheology at 1% strain from 0.1-100 Hz. The black line represents the transition region between bulk deformation that leads to Saffman-Taylor fingering instability (above the line) and interfacial crack propagation (below the line) as outlined in Nase et al. 11.

According to Nase et al. 11, both our PSAs lie in the range of bulk deformation leading to the formation of fingers (see Figure S7). We use the current analysis for 5% AA PSA. The same analysis cannot be carried out for 0%AA due to the presence of cavitation before fingering during debonding of PSA in 0%AA in water. As seen in Figure S8, $(\lambda \sqrt{U})^2$ obtained from in situ image analysis during the debonding process is proportional to the surface energy of the PSA determined from contact angle measurements. It is surprising that equation S19 appears to hold for the PSA, as it contains several assumptions that have been outlined before 11, in particular, one being treating the PSA as Newtonian fluid during fingering. Unfortunately, we cannot obtain absolute values of the surface energy for the PSA using this method without performing a more detailed analysis bulk fingering of a viscoelastic solid, such analysis will be the subject of future investigations.
**Figure S8.** Surface energy of 5% AA PSA-water interface calculated using receding contact angle measurements vs \((\lambda\sqrt{U})^2\) obtained from fingering wavelength analysis for Saffman-Taylor instabilities with the dashed line shown to depict proportionality.

**Table S7.** Comparison of surface energy of 5% AA in solution \((\gamma_{13})\) calculated using contact angle measurements as shown in Table S3 with \((\lambda\sqrt{U})^2\) from in-situ fingering wavelength analysis as shown in equation S19.

| pH | \(\gamma_{13}\) (mJ/m\(^2\)) | \((\lambda\sqrt{U})^2 \times 10^{-6}\) (\(\mu m^3/s\)) |
|----|-----------------|-----------------|
| 3  | 13 ± 3          | 5.1 ± 1.2       |
| 6  | 12 ± 2          | 3.9 ± 0.8       |
| 8  | 9 ± 3           | 2.1 ± 0.5       |
| 11 | 4 ± 1           | 1.3 ± 0.4       |

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