

Sea-surface retention effect shapes ocean microplastic fibers

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Microfibers contaminate the global ocean, but their impact depends on length-dependent residence at the air-sea interface. In the submillimeter range, the sea surface exhibits a surface-enrichment signature: The long-to-short fiber ratio is higher at the interface than a few meters below (about 5 m), meaning that longer fibers are relatively more represented at the surface, despite an approximately length-flat fragment production expected below the fiber breakage cutoff. We show that this contrast is consistent with length-selective retention in the sea-surface microlayer via capillary pinning and attachment to sparse anchoring sites. A minimal two-state mixed-layer column model yields an approximately linear surface enrichment, reproduces the observed surface-subsurface contrast, and identifies the microlayer as a dynamic reservoir shaping residence times, exposure, and air-sea exchange of fiberlike pollutants.

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I. INTRODUCTION

Microplastic fibers are now recognized as a pervasive contaminant from coastal seas to the open ocean and often dominate particle counts in near-surface samples [1,2]. Their environmental relevance, however, is not captured by abundance alone. Fibers are elongated, flexible particles, and particle morphology is increasingly recognized as a first-order control on environmental fate [3]. The upper ocean is a particularly critical setting because it hosts both the first contact with planktonic communities and the air-sea boundary, where oceanic, ecological, and atmospheric pathways intersect [4–6].

A central open issue is therefore not merely “how many fibers,” but which lengths reside where in the upper ocean. Fiber length is a dynamically and ecologically relevant state variable: It controls encounter and ingestion pathways for plankton and other surface-dwelling organisms through size- and shape-dependent contact rates [4]; it affects how fibers interact with flow, orient, tumble, and settle [7]; and it conditions the likelihood of transfer across the air-sea boundary via bubbles and droplets generated by breaking waves [5]. In practice, the same total concentration can imply very different consequences if the population is concentrated in the top millimeters, where interfacial processing and exposure are strongest, or diluted a few meters below. A mechanistic description of length-resolved vertical partitioning is

therefore needed to connect observations, ecological exposure, and transport across oceanic compartments.

Yet, this is precisely where our understanding remains fragmentary. Many marine surveys report total abundance, polymer type, and broad shape classes, but much less is known about how fiber-length spectra are reshaped between the air-sea interface and the underlying mixed layer. Recent syntheses show that subsurface microplastic distributions can differ markedly from what surface sampling alone would suggest, and that particle size is a key control on this vertical structure [8]. At the same time, the sea-surface microlayer (SML) is increasingly recognized as a physically and biogeochemically distinct boundary layer rather than a passive sampling surface [6]. Field and experimental studies further suggest that fibers can be selectively retained or enriched there through capillary, adhesive, and gel-mediated processes [9,10]. What is still missing, however, is a simple theoretical framework that explains how an interface-localized reservoir can selectively reshape the observed fiber-length spectrum at the surface while leaving the subsurface spectrum comparatively flat over the same submillimeter range.

This gap matters for at least two reasons. First, without a process-based interpretation, surface observations risk being read only in terms of source strength or net accumulation, even when they may instead reflect length-dependent partitioning between a freely suspended pool and an interface-bound reservoir. Second, large-scale transport models require compact closures for length-dependent residence if they are to predict exposure, dispersion, and air-sea exchange realistically. Although theoretical and numerical work on microplastics is growing, reviews emphasize that morphology is still insufficiently represented in fate studies [3]; explicit, process-based modeling focused on fibers remains comparatively scarce, with recent examples addressing mainly settling in water or long-range transport in air [7,11]. In this sense, the present study belongs to the still limited group

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of theory-driven efforts aimed specifically at a fiber-selective mechanism in the marine environment.

In this paper, we address that gap by focusing on the near-surface ocean as a coupled two-state system. We first revisit paired surface and subsurface observations from the Antarctic Circumnavigation Expedition (ACE) and show that, in the submillimeter range, the sea surface exhibits a robust enrichment toward longer fibers relative to samples taken a few meters below [1]. We then compare this constraint with independent datasets showing the same qualitative tendency [12,13]. Motivated by these observations, we introduce a minimal mechanistic model in which freely suspended fibers in the upper mixed layer exchange with an interface-localized reservoir in the SML through length-dependent attachment and detachment. We show that this picture naturally yields an approximately linear surface enrichment, reconciles the contrast between surface and subsurface spectra, and provides a compact parametrization of length-dependent surface residence that can be embedded in larger-scale models of fiber dispersion and air-sea exchange.

II. EVIDENCE FOR SURFACE ENRICHMENT

To motivate the theoretical framework developed below, we first establish the observational constraint that the model must explain. We begin with a reanalysis of the paired ACE surface and subsurface measurements, which makes the length-dependent surface enrichment quantitatively explicit in the submillimeter range, and then compare this pattern with independent datasets showing the same qualitative tendency. The goal of this section is therefore to identify the empirical signature to be explained: a surface fiber-length spectrum selectively enriched in longer fibers relative to the underlying water.

A. ACE reanalysis

Against this backdrop, a striking observational constraint has emerged in the submillimeter range: Relative to measurements a few meters below the surface, sea-surface samples show a higher long-to-short fiber ratio (i.e., a length-dependent surface enrichment, with the shortest classes underrepresented) [1,14], whereas subsurface spectra are appreciably flatter and small sizes re-emerge [2,8]. A reanalysis of the ACE dataset [1], presented in Fig. 1, makes this conclusion quantitatively explicit. This is possible because ACE includes paired surface (bucket) and subsurface intake samples at a depth of $H \simeq 5$ m collected under the same cruise conditions. A further advantage of ACE is that campaign-scale meteorological forcing (including wind statistics) is reported [15], enabling physically grounded mixed-layer scaling estimates. Figure 1 (upper panel) overlays the ACE surface and subsurface fiber-length probability density functions (PDFs), $p_0(L)$ and $p_H(L)$, i.e., the normalized length spectra at the surface ($z = 0$) and at the intake depth ($z = H \simeq 5$ m), using the same logarithmic bins. These PDFs are obtained from the number spectra $n(z, L)$ (fibers per unit volume and per unit length) via $p_z(L) = n(z, L) / \int n(z, s) ds$, so that the comparison isolates spectral shape independently of the total concentration. Two features are worth emphasizing.

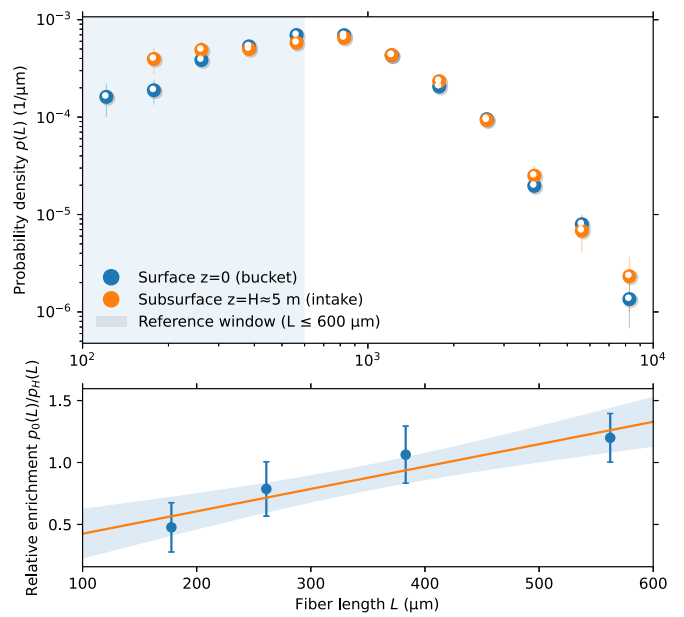


FIG. 1. Upper panel: ACE fiber-length PDFs at the sea surface ($z = 0$, bucket) and subsurface intake depth ($z = H \simeq 5$ m) [1], estimated in the same $N_b = 12$ logarithmic bins; error bars are 1σ Poisson counting uncertainties. Lower panel: Shape-based relative enrichment $R(L) \equiv p_0(L_i)/p_H(L_i)$ in the same bins, with uncertainties propagated from independent Poisson errors; a weighted linear fit for $L_i \leq 600 \mu\text{m}$, $R(L) = a + bL$ (with L in μm), gives $a = 0.3 \pm 0.3$ and $b = (1.8 \pm 0.7) \times 10^{-3} \mu\text{m}^{-1}$ (1σ), with $\chi^2/\text{dof} = 0.351$ ($\text{dof} = 2$). Total raw counts are $N_0 = 930$ (surface) and $N_H = 408$ (subsurface).

First, both PDFs exhibit a broad maximum in the few-hundred-micron range; this reflects the fact that fiber-length distributions are not pure power laws across decades. The reduced model developed below is not intended to reproduce that full nonmonotonic shape over the entire plotted range; rather, it isolates the local surface-subsurface reshaping within the conservative submillimeter window, where the supply can be treated as approximately length flat to leading order. Second, within a conservative submillimeter reference window (shaded, $L \leq 600 \mu\text{m}$), the surface PDF is relatively enriched in longer fibers compared with the subsurface PDF (i.e., the long-to-short ratio is higher at the surface). This is quantified in Fig. 1 (lower panel), which shows the shape-based ratio $R(L_i) \equiv p_0(L_i)/p_H(L_i)$ in common bins where both depths have nonzero counts, where L_i denotes the representative length of the i th logarithmic bin (taken as the bin geometric mean). A linear best fit $R(L) = a + bL$ (with L in μm) yields $a = 0.3 \pm 0.3$ and $b = (1.8 \pm 0.7) \times 10^{-3} \mu\text{m}^{-1}$ (1σ). Across the fitted window, this corresponds to a change in $R(L)$ by roughly a factor of 2–3 from the shortest to the longest populated classes, i.e., an order-unity reshaping of the normalized surface spectrum relative to the subsurface one. Thus, even though both PDFs peak at comparable scales, the surface-to-subsurface enrichment increases linearly with L across the reference window, indicating a relative depletion of shorter fibers and a relative overrepresentation of longer fibers at the interface. A complementary view is provided by the compensated representation in Fig. 2 where the surface spectrum

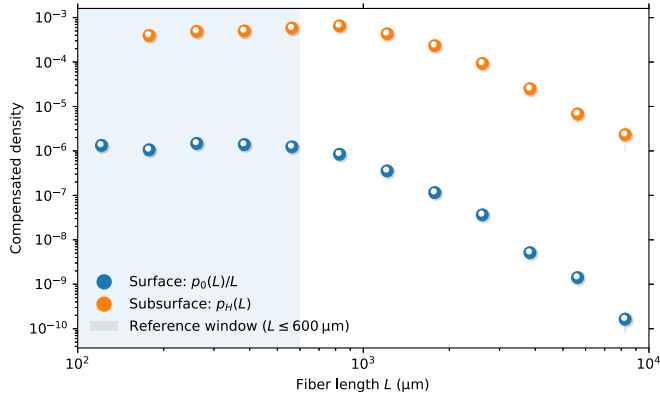


FIG. 2. Same datasets and common logarithmic binning as in Fig. 1. Compensated overlay of the two PDFs over the full plotted range $L \in [10^2, 10^4] \mu\text{m}$ using different compensation factors that reflect the empirical scaling trends discussed in the main text. Error bars represent 1σ Poisson counting uncertainty propagated through the compensation factors.

is compensated by L (we plot $p_0(L_i)/L_i$), while the subsurface spectrum is left uncompensated (we plot $p_H(L_i)$). This compensated representation is not intended as an independent observable, but as a compact diagnostic of whether the leading surface trend is removed by the L compensation suggested by Fig. 1. If the surface enrichment is approximately proportional to L over the window, compensating the surface spectrum by L should eliminate its systematic L trend. Figure 2 shows that this is the case, confirming that the incremental surface enrichment is approximately linear in L in the submillimeter regime.

B. Independent datasets

As a robustness check of the surface enrichment observed in Figs. 1 and 2, we also considered two additional, independent, and very recent datasets: CALYPSO FTIR [12], collected during the 2022 CALYPSO oceanographic campaign in the Balearic Sea (western Mediterranean) and based on vertically resolved seawater sampling across a submesoscale cyclonic eddy, and the TJJMS dataset [13], a coastal survey around Japan (spanning from Hokkaido to Okinawa) conducted between 2022 and 2023 that reports microfiber sizes from surface-water samples collected with a Neuston net. The corresponding PDFs from surface-water samples (TJJMS dataset) and from pooling across all available depths (CALYPSO FTIR) are shown in Fig. 3. The trends of the two curves (orange and blue symbols) are qualitatively consistent with a surface-enrichment signature: Within the submillimeter window (up to about 1 mm), the surface spectrum (blue) increases with fiber length and is relatively enriched in longer fibers compared with the pooled-depth spectrum (orange), which is appreciably flatter. Because these datasets are not paired surface-subsurface measurements obtained under the same sampling protocol, we use them only as qualitative support for a surface-biased trend, not as a quantitative test of the ACE-derived linear law.

While these independent datasets are consistent with the same qualitative surface-biased trend, we do not claim strict

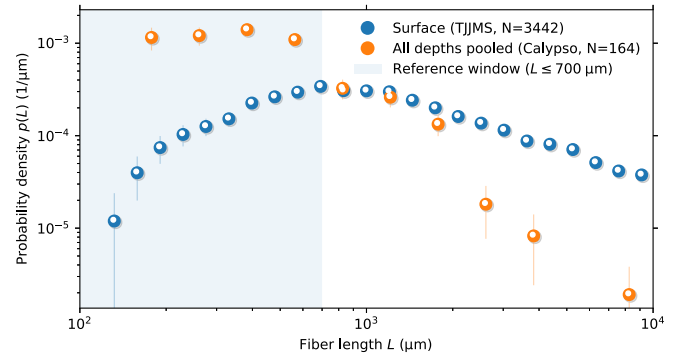


FIG. 3. The PDF of microfiber length L is computed by combining two independent datasets, CALYPSO FTIR [12] and TJJMS [13]. Orange markers are obtained from the CALYPSO FTIR dataset by pooling all fibers collected at the different available depths. Blue markers are obtained from the TJJMS dataset, which corresponds to surface sampling (Neuston net). Error bars, as well as the choice of the number of bins and their spacing, are defined as in Fig. 1.

universality, because the available campaigns do not provide concomitant measurements of SML physicochemical properties (e.g., gel/TEP and surfactant enrichment) that would be needed to assess how retention depends on microlayer “stickiness.” Rather, our results strongly motivate future paired surface-subsurface surveys that couple fiber spectra to such SML diagnostics.

III. MICROLAYER RETENTION MODEL

Taken together, the paired ACE constraint (Figs. 1 and 2) and the independent evidence in Fig. 3 sharpen the central question of this paper: What near-surface mechanism can selectively reshape the fiber-length spectrum at the interface, while leaving the subsurface spectrum comparatively flat over the same submillimeter range? A purely measurement-related explanation for the ACE observation appears unlikely, because surface and intake samples were processed with the same filtration protocol [1], and the additional datasets in Fig. 3 involve different platforms (a vertically resolved conductivity-temperature-depth (CTD) rosette/Niskin-bottle water-column protocol versus surface Neuston-net sampling) yet exhibit consistent surface-biased trends. A second, physically natural hypothesis is that a length-dependent air-sea exchange flux (deposition/ejection) could imprint a surface trend. However, under the rapid near-surface mixing conditions relevant to paired surface-subsurface comparisons, any boundary forcing acting on the freely suspended population is rapidly redistributed across the top few meters and therefore cannot produce a surface-only change in spectral shape while leaving the subsurface spectrum comparatively unchanged. We anticipate this point here and return to it below, where we quantify the mixed-layer regime and show that vertical mixing over $H \simeq 5\text{ m}$ is fast compared with settling and bulk removal of fibers. This points to an additional interface-localized reservoir that contributes to what surface sampling collects but is largely absent from a subsurface intake. The SML provides a natural candidate for such a reservoir. It is enriched in surfactants, gels, and

microbial material, and can host capillary and adhesive interactions that transiently bind particles at the interface. While direct open-ocean *in situ* quantification of fiber-scale attachment statistics and their length dependence is still largely lacking, several independent observations motivate the existence of localized anchoring features: Estuarine SML studies report strong microfiber enrichment and scanning electron microscopy reveals fibers bearing adhered sediment and diatom cells [9], consistent with discrete attachment points; coastal SML samples indicate that sticky microgels and surface tension can keep even dense particles afloat, with a substantial fraction remaining at the surface after vigorous stirring in beaker tests [10]; early biofilms develop as patchy microcolonies rather than uniform coatings [16,17], and the SML is enriched in transparent exopolymer particles (TEPs), with enrichment driven by bubble scavenging [18]; and bubble-microplastic attachment has been quantified in flotation experiments [19]. These ingredients motivate a minimal statistical picture: A fiber at the interface has multiple, approximately independent opportunities to pin or attach to localized anchors, so that longer fibers have more chances to engage at least one anchor. Below we formalize this picture and show that an interface-localized reservoir can simultaneously account for the observed, approximately linear surface enrichment and for the comparatively flat subsurface spectra.

A. Two-state exchange

To do so, we resolve the near-surface population at fixed fiber length L into two coupled states and embed them in a minimal one-dimensional (1D) column model for the top H meters. We use the vertical coordinate z measured positive downward, with $z = 0$ at the mean air-sea interface and $z = H$ the subsurface intake depth (for ACE, $H \simeq 5$ m). The freely suspended population in the upper ocean is described by a number spectrum $c(z, L, t)$ (fibers per unit volume and per unit length) for $0 < z \leq H$. In addition, we introduce an interface-localized reservoir retained in the SML, described by an areal spectrum $b(L, t)$ (fibers per unit area and per unit length) concentrated at $z = 0$. We now relate these state variables to the observable length spectra $n(z, L)$ introduced above. In particular, the ship's underway intake at $z = H$ draws subsurface water and therefore samples only the freely suspended pool, so that

$$n(H, L) = c(H, L). \quad (1)$$

A surface bucket, in contrast, necessarily collects (1) a volume of near-surface water containing freely suspended fibers and (2) the interfacial film itself, in which fibers can reside in an interface-bound state. We represent the bucket collection as an effective entrainment thickness δ of underlying water plus the conversion of the areal interfacial density $b(L)$ into an equivalent volumetric contribution $b(L)/\delta$, which yields

$$n(0, L) = c(0, L) + \frac{b(L)}{\delta}. \quad (2)$$

Here, δ is an effective sampling thickness converting the areal interfacial content into the equivalent volumetric contribution collected by the bucket; it is set by the collection geometry and protocol and should not be interpreted as the physical

thickness of the sea-surface microlayer itself. Equation (2) makes explicit why the surface and subsurface spectra can differ in shape even when the freely suspended pool is nearly well mixed: The bucket includes an additional interface-bound contribution that the subsurface intake does not sample.

The interface-bound reservoir exchanges fibers with the freely suspended pool through attachment and detachment fluxes at $z = 0$, denoted as $J_{\text{on}}(L, t)$ and $J_{\text{off}}(L, t)$ (fibers per unit area, time, and length). Over the submillimeter window, we neglect interfacial fragmentation within the reservoir (see Appendix A) and model its kinetics as

$$\partial_t b(L, t) = J_{\text{on}}(L, t) - J_{\text{off}}(L, t). \quad (3)$$

This approximation is justified by the ACE turbulence-limited breakage threshold L_{brk} , defined as the fiber length above which turbulent bending stresses can exceed the material strength [20]. Appendix A shows that, under ACE dissipation brackets and for the dominant fiber classes, L_{brk} is in the inertial range and lies at centimetric scales, $L_{\text{brk}} = O(10\text{--}30)$ cm, at both the surface and $z = H$. Since our analysis focuses on $L \lesssim 1$ mm $\ll L_{\text{brk}}$, turbulence-mediated breakage of submillimeter fibers is not expected to be active in the SML, so that SML dynamics over this window are dominated by exchange (capture/detachment) rather than by interfacial fragmentation. To close the fluxes J_{on} and J_{off} , we do not fit an arbitrary functional form to the data; rather, we adopt a minimal, process-motivated closure and then use the observations only as a diagnostic check.

To be more specific, we model effective attachment/pinning opportunities in the SML as localized anchoring sites distributed along a fiber with constant linear density λ (m^{-1}), and assume approximately independent sites (Poisson in length). Under this assumption [21], the probability that at least one anchoring site is available along a fiber of length L is

$$P_{\geq 1}(L) = 1 - e^{-\lambda L} \simeq \lambda L, \quad (4)$$

where the linear approximation holds in the dilute-anchor regime $\lambda L \lesssim 1$, a condition that we later verify *a posteriori* for the fitted submillimeter window. Attachment also requires that a near-surface fiber is delivered to and contacts the interface with a favorable configuration; rather than resolving the detailed orientation and interfacial-renewal dynamics, we lump near-surface delivery and sticking efficiency into an effective interfacial transfer velocity ν (units m s^{-1}). In this factorization, ν accounts for delivery/contact to the interface, whereas anchoring statistics enter only through the probability that such contact results in successful capture. The attachment flux per unit area, time, and unit length is then $J_{\text{on}}(L) = \nu P_{\geq 1}(L) c(0, L)$, and using Eq. (4) it reads

$$J_{\text{on}}(L) = r_{\text{on}}(L) c(0, L) \simeq k_{\text{on}} L c(0, L), \quad k_{\text{on}} \equiv \nu \lambda, \quad (5)$$

where $r_{\text{on}}(L)$ is the effective interfacial attachment (capture) coefficient that converts the near-surface volumetric spectrum $c(0, L)$ into an areal attachment flux. It then follows that $J_{\text{on}} \propto L$ because, in the regime (4), doubling the fiber length approximately doubles the number of independent anchoring opportunities. Detachment is expected to be hysteretic at the microscale (contact-line pinning, intermittent renewal, and history-dependent adhesive contacts), so we do not attempt

a microscopic threshold model. Instead, we coarse grain these details into an effective detachment hazard k_{off} (s^{-1}): On timescales longer than the microscopic renewal time, each bound fiber has an approximately constant probability per unit time to detach, which yields the first-order flux

$$J_{\text{off}}(L) = k_{\text{off}} b(L). \quad (6)$$

Treating k_{off} as only weakly length dependent is physically motivated because, in the regime relevant to the observed near-linear enrichment, detachment is expected to be controlled by breaking an $O(1)$ number of contacts. This assumption is corroborated *a posteriori* by the dilute-anchor consistency bound implied by the observed approximately linear enrichment trend. Specifically, the dilute-anchor assumption underlying Eq. (4) implies that the bound population is dominated by single-anchor events; if $N \sim \text{Poisson}(\lambda L)$ is the number of potential anchors along a fiber and a fiber is bound only if $N \geq 1$, then

$$\mathbb{E}[N | N \geq 1] = \frac{\lambda L}{1 - e^{-\lambda L}} \simeq 1 + \frac{\lambda L}{2} + O((\lambda L)^2), \quad (7)$$

so for $\lambda L \ll 1$ the typical bound fiber carries $O(1)$ anchors. In this single-anchor-dominated regime, detachment is governed mainly by the physics of breaking one contact. More generally, the observations constrain the increase of $J_{\text{on}}/J_{\text{off}}$ with L ; the present closure is the minimal capture-controlled realization of that trend implied by the dilute-anchor picture.

On timescales long compared with the exchange time, the reservoir is close to steady exchange at each L and Eq. (3) yields $J_{\text{on}}(L) \simeq J_{\text{off}}(L)$. Using Eqs. (5) and (6) gives

$$b(L) = \frac{k_{\text{on}}}{k_{\text{off}}} L c(0, L). \quad (8)$$

Substituting Eq. (8) into the sampling relation (2) yields the measurable surface-enrichment law

$$n(0, L) = c(0, L) [1 + \alpha L], \quad \alpha \equiv \frac{k_{\text{on}}}{k_{\text{off}} \delta}, \quad (9)$$

which isolates the SML imprint into a single length-selective enrichment parameter α (m^{-1}). Physically, α^{-1} is the crossover length at which the interface-bound contribution b/δ becomes comparable to the freely suspended contribution $c(0, L)$ in a surface bucket sample, since $b(L)/\delta = \alpha L c(0, L)$. From the fit in Fig. 1, we obtain $\alpha^{-1} \sim O(10^2) \mu\text{m}$, implying $\alpha L = O(1-4)$ over $L \simeq 200-600 \mu\text{m}$. Thus, over the fitted submillimeter window the interface-bound contribution is $O(1)$ relative to the freely suspended pool (and can dominate for longer fibers), explaining a surface-only reshaping despite a well-mixed free pool.

B. Mixed-layer column

We now embed this two-state exchange in a minimal column model for the freely suspended pool in $0 < z \leq H$. We represent the vertical transport of $c(z, L, t)$ by turbulent diffusion with constant eddy diffusivity K and by an effective settling/rising speed w_s (positive downward). We define the total downward vertical flux of freely suspended fibers as

$$F(z, L, t) \equiv -K \partial_z c(z, L, t) + w_s c(z, L, t). \quad (10)$$

The bulk pool then satisfies the 1D advection-diffusion-reaction balance

$$\partial_t c(z, L, t) = -\partial_z F(z, L, t) - k(L) c(z, L, t) + S_0 \quad (11)$$

for $0 < z \leq H$, or equivalently

$$\partial_t c = \partial_z (K \partial_z c) - \partial_z (w_s c) - k(L) c + S_0. \quad (12)$$

Here, $k(L)$ (s^{-1}) is the bulk first-order removal rate from the freely suspended pool within the layer (exclusive of SML exchange), collecting irreversible bulk losses (e.g., aggregation and biofouling-driven conversion to sinking states) as well as effective exchange with deeper layers not represented explicitly by the boundary condition; S_0 is an effective length-independent volumetric input within the resolved layer $0 < z \leq H$, representing the approximately flat submillimeter supply after coarse graining below the fragmentation cutoff L_{brk} under equiprobable scission (see Appendix B); and K is a mixed-layer diffusivity [22]. We stress that the argument does not require $k(L)$ to be strictly constant, only weakly L dependent across the fitted submillimeter window. The fact that w_s is only weakly length dependent does not by itself force $k(L)$ to be constant; rather, it implies that the most direct advective contribution $|w_s|/H$ to bulk loss varies at most logarithmically with L . Together with the ACE-based mixed-layer bounds in Appendix C, this motivates treating $k(L)$ as only weakly length dependent across $10^2-10^3 \mu\text{m}$, so that its residual variation is subdominant compared with the linear SML factor $1 + \alpha L$ in Eq. (9). The boundary condition at the base of the layer is no net flux,

$$F(H, L, t) = 0, \quad (13)$$

which closes the top- H control volume for the explicitly resolved transport; any net transfer to depths $>H$ is parametrized by the bulk loss rate $k(L)$. At the interface, the freely suspended pool is forced by net air-sea exchange (atmospheric deposition minus ejection) and it exchanges fibers with the SML reservoir. We represent the net air-sea exchange by a flux $\Phi_{\text{air}}(L, t)$ (fibers per unit area, time, and length), taken positive when it injects fibers into the ocean. Conservation of the freely suspended pool then implies the surface flux condition

$$F(0, L, t) = \Phi_{\text{air}}(L, t) + J_{\text{off}}(L, t) - J_{\text{on}}(L, t). \quad (14)$$

The term $J_{\text{off}} - J_{\text{on}}$ is the net exchange from the SML reservoir back into the freely suspended pool; it vanishes under steady SML exchange ($J_{\text{on}} = J_{\text{off}}$), in which case the boundary condition for the free pool reduces to $F(0, L) = \Phi_{\text{air}}(L)$. This makes explicit the separation stressed above: In the paired ACE regime, the reservoir does not need to provide a net source/sink of the freely suspended pool to reshape the *observed* surface spectrum; its effect enters through the sampling operator (2). The net air-sea exchange $\Phi_{\text{air}}(L, t)$ is therefore conceptually distinct from S_0 : Φ_{air} is a boundary flux at $z = 0$, whereas S_0 is a distributed volumetric source within the resolved layer. The no-flux condition at $z = H$ in Eq. (13) closes only the explicitly resolved advective-diffusive transport and is fully consistent with $S_0 \neq 0$. In the fast-mixing regime, any approximately length-flat, or only weakly length-dependent, net air-sea contribution is rapidly homogenized over the layer

and enters the layer-mean balance as Φ_{air}/H ; to leading order over the fitted window, such a term may therefore be absorbed into an effective source $S_0^{\text{eff}} = S_0 + \Phi_{\text{air}}/H$ without affecting the surface-subsurface shape contrast. For notational simplicity, we absorb any such contribution into S_0 in the reduced expressions below. A size-selective air-sea exchange, including preferential ejection of shorter fibers, may therefore modify the layer-mean spectrum of the freely suspended pool, but in the fast-mixing regime it does not replace the need for an interface-localized reservoir to explain a surface-only bucket/intake shape contrast.

In the mixed-layer regime relevant to paired surface-subsurface observations, vertical mixing is fast compared with weak settling and bulk removal across the top H meters. This is quantified by the Péclet number $\text{Pe} \equiv |w_s|H/K$ and the Damköhler number $\text{Da} \equiv k(L)H^2/K$, which are both small under ACE conditions (see Appendix C). In this regime, the solution of the steady version of Eq. (12) is nearly uniform over $0 < z \leq H$,

$$c(z, L) \simeq \frac{S_0}{k(L)} [1 + O(\text{Pe}, \text{Da})], \quad 0 < z \leq H, \quad (15)$$

so that $c(0, L) \simeq c(H, L)$ to leading order and the subsurface intake samples

$$n(H, L) = c(H, L) \simeq \frac{S_0}{k(L)}. \quad (16)$$

Because $k(L)$ varies only weakly with L across the submillimeter window (at most logarithmically, as argued above and supported by the bounds reported in Appendix C), Eq. (16) is consistent with an approximately flat subsurface spectrum over the conservative reference range. In contrast, combining Eq. (9) with Eq. (15) gives

$$n(0, L) \simeq \frac{S_0}{k(L)} [1 + \alpha L], \quad (17)$$

i.e., an interface spectrum that increases with L once αL is not small. Equivalently, the effective surface kernel mapping the flat injection S_0 to the observed surface spectrum is

$$k_{\text{surf}}(L) \equiv \frac{S_0}{n(0, L)} = \frac{k(L)}{1 + \alpha L} \sim L^{-1} \quad \text{for } \alpha L \gg 1, \quad (18)$$

which is the fingerprint of the length-selective mechanism. Accordingly, the surface-subsurface shape contrast does not rely on a proliferation of fitted length-dependent functions: S_0 fixes the background level of the freely suspended pool, while the only additional length-selective factor is $1 + \alpha L$.

IV. CONSISTENCY CHECKS

We conclude this paper by discussing internal consistency checks of the proposed mechanism against the ACE-based constraints. Using the fit-derived value of α^{-1} discussed above, we have already quantified the critical length scale at which the interface-bound contribution becomes comparable to the freely suspended one in a surface bucket sample, since $b(L)/\delta = \alpha L c(0, L)$. This immediately implies that the SML reservoir provides an $O(1)$ contribution over the fitted submillimeter window and can therefore account for a surface-only reshaping despite a well-mixed free pool.

The approximately linear dependence of the shape-based enrichment $R(L) = p_0(L)/p_H(L)$ over the conservative window is also consistent with the dilute-anchors regime used to justify $P_{\geq 1}(L) \simeq \lambda L$: The absence of visible saturation in $R(L)$ over the fitted window in Fig. 1 (lower panel) suggests $\lambda L \lesssim 1$ across the window, which implies

$$\lambda \lesssim \frac{1}{L_{\text{max}}} \sim \frac{1}{600 \mu\text{m}} \simeq 1.7 \times 10^3 \text{ m}^{-1}, \quad (19)$$

corresponding to a mean anchor spacing $\gtrsim O(\text{mm})$.

Finally, the fitted α can be combined with a geometric estimate of the bucket entrainment thickness to obtain an order-of-magnitude constraint on the interfacial partitioning. Writing $\delta \simeq V/A$ and estimating the effective collection area by $A \simeq V^{2/3}$ (bucketlike geometry) gives $\delta \simeq V^{1/3}$. For a typical ACE surface sample volume $V \simeq 10 \text{ L} = 1 \times 10^{-2} \text{ m}^3$ [1], this yields $\delta \simeq 0.22 \text{ m}$ and therefore

$$\frac{k_{\text{on}}}{k_{\text{off}}} = \alpha \delta \sim (7 \times 10^3 \text{ m}^{-1}) \times (0.22 \text{ m}) \sim 10^3. \quad (20)$$

We stress that δ is an effective bucket entrainment thickness, not the physical thickness of the SML itself. Equation (20) therefore constrains the interfacial partitioning sampled by the collection protocol. Moreover, Eq. (20) constrains only the ratio $k_{\text{on}}/k_{\text{off}}$, not the two rates separately. Nevertheless, the inferred ratio is compatible with reasonable kinetic values. Using $\lambda \lesssim 1.7 \times 10^3 \text{ m}^{-1}$ from Eq. (19) and a conservative effective interfacial transfer velocity $\nu \sim 10^{-5}$ to 10^{-4} m s^{-1} gives $k_{\text{on}} = \nu \lambda \sim 10^{-2}$ to 10^{-1} s^{-1} . Equation (20) then implies $k_{\text{off}} \sim 10^{-5}$ to 10^{-4} s^{-1} , corresponding to bound-state residence times of a few hours to about a day. For a representative fiber length $L \sim 3 \times 10^{-4} \text{ m}$, the corresponding capture velocity is $r_{\text{on}}(L) = k_{\text{on}} L \sim 10^{-6}$ to 10^{-5} m s^{-1} , which is physically reasonable for an effective interfacial retention process. Thus, the ACE-inferred partitioning does not require extreme kinetic values. Even allowing an order-unity geometric uncertainty in δ , the inferred ratio $k_{\text{on}}/k_{\text{off}}$ remains $O(10^3)$. Together, Eqs. (19) and (20) and the order-of-magnitude estimate above show that the ACE-inferred length selectivity is consistent with a dilute-anchor microlayer reservoir. These estimates also suggest clear priorities for future field work: Colocated SML and underlying-water measurements of length-resolved fiber spectra, repeated in time under varying wind and sea-state conditions, could directly constrain the interfacial partitioning (and potentially disentangle k_{on} and k_{off}). Crucially, such measurements should be paired with diagnostics of SML composition and “stickiness” (gel-like material/TEP, surfactants, and biofilm proxies), to test whether the inferred crossover scale and length selectivity strengthen when the microlayer is enriched in adhesive constituents, as expected if retention is mediated by localized anchoring and pinning.

V. CONCLUSIONS AND PERSPECTIVES

In conclusion, this work identifies a clear and physically meaningful near-surface constraint on ocean microplastic fibers: In the submillimeter range, the fiber-length spectrum sampled at the sea surface is selectively shifted toward longer fibers relative to the spectrum a few meters below. Within the

observational window considered here, this reshaping is well captured by an approximately linear surface enrichment with fiber length. Independent datasets support the same qualitative tendency, indicating that the ACE pattern is unlikely to be an isolated feature of a single campaign. At the same time, mixed-layer scaling supports a picture in which the freely suspended population over the top few meters is nearly well mixed and only weakly affected by length-dependent bulk removal. This combination of facts points naturally to an interface-localized reservoir as the missing ingredient needed to explain why the observed surface spectrum can differ in shape from the subsurface one.

The minimal two-state framework introduced here shows that such a reservoir can arise from selective retention in the sea-surface microlayer. In this picture, freely suspended fibers exchange with an interface-bound population through attachment and detachment, and longer fibers are preferentially retained because they have more opportunities to interact with sparse anchoring sites. This mechanism simultaneously explains two features that would otherwise be difficult to reconcile: the comparatively flat subsurface spectrum and the surface enrichment toward longer fibers. The resulting closure is intentionally compact, but it is already rich enough to provide a process-based interpretation of observations and a practical parametrization for transport models.

The broader interest of these results is that they shift the interpretation of sea-surface microplastic measurements from a purely concentration-based view to a partitioning-based one. Surface samples do not simply report how many fibers are present in the upper ocean; they may also encode how fiber geometry and interfacial physics redistribute the population between a freely suspended mixed-layer pool and an interface-bound microlayer reservoir. This distinction matters because the topmost ocean is the layer most directly connected to biological exposure, photochemical and mechanical processing, and exchange with the atmosphere. A length-selective surface residence time can therefore alter ecological encounter rates, bias the size structure of what is available for bubble-mediated transfer, and modify how fiber pollution is communicated between oceanic and atmospheric compartments.

More generally, the present results highlight a point of broad relevance for fiberlike pollutants: Particle shape is not a secondary detail, but a dynamical variable that can control environmental fate through interfacial interactions. In this sense, the framework developed here is not only a contribution to marine microplastic studies, but also part of a wider effort to build theory-guided descriptions of how anisotropic particles are sorted and retained in natural boundary layers. The sea-surface microlayer emerges from this work not as a passive observational boundary, but as an active and selective reservoir capable of reshaping pollutant spectra.

Several perspectives follow directly. On the observational side, the most urgent need is for systematic paired measurements of the microlayer and the underlying water, repeated under different wind, wave, and biological conditions, and combined with diagnostics of microlayer composition and “stickiness” such as surfactants, gels, transparent exopolymer particles, and biofilm proxies. Such datasets would allow the interfacial partitioning to be constrained directly and would test whether the inferred crossover scale and length selectivity

strengthen under more adhesive microlayer conditions. On the modeling side, the natural next step is to embed the present closure into regional and global transport models, so that fiber length becomes an explicit prognostic variable in predictions of near-surface residence, dispersion, and air-sea exchange. Extensions that include transient forcing, saturation of anchoring opportunities, evolving biofilm coverage, and coupling to bubble scavenging and aerosolization are especially promising.

Taken together, these results suggest that the upper ocean retains a memory of particle geometry through interface-selective residence. Recognizing and parametrizing this effect can improve how observations are interpreted, refine how exposure pathways are assessed, and provide a missing link between field measurements and predictive models of fiber pollution in the coupled ocean-atmosphere system.

DATA AVAILABILITY

The data that support the findings of this article are openly available in the Supplemental Material of Ref. [1].

APPENDIX A: ACE TURBULENCE SCALE AND TURBULENCE-LIMITED BREAKAGE

This Appendix summarizes the ACE-based estimates used in the main text to exclude active turbulence-mediated fragmentation in the submillimeter window. ACE paired surface bucket samples with underway-intake samples at $H \simeq 5$ m [1]; the expedition-wide median wind was $U_{10} = 7.25 \text{ m s}^{-1}$ [15]. Using $C_D = 1.3 \times 10^{-3}$, $u_{*a} = \sqrt{C_D} U_{10}$, and stress continuity across the interface gives a water-side friction velocity $u_{*w} \simeq 9 \times 10^{-3} \text{ m s}^{-1}$ [23]. We estimate the wave-affected dissipation rate as

$$\varepsilon_t(z) = \xi \frac{u_{*w}^3}{\kappa z}, \quad (\text{A1})$$

where $\kappa = 0.4$ and $\xi = 20\text{--}100$ brackets moderate breaking or microbreaking conditions [24,25]. With the water kinematic viscosity denoted by ν_w , the Kolmogorov length is

$$\eta = \left(\frac{\nu_w^3}{\varepsilon_t} \right)^{1/4},$$

$$\eta(0.2 \text{ m}) \simeq 0.18\text{--}0.27 \text{ mm},$$

$$\eta(5 \text{ m}) \simeq 0.40\text{--}0.61 \text{ mm}, \quad (\text{A2})$$

where the 5 m estimate follows from the same scaling with the dissipation reduced by a factor $\simeq 25$.

The dominant ACE fiber classes are cellulosic fibers, with natural animal fibers as the next most frequent class [1]. We use the representative median fiber diameter

$$d = 16.7 \mu\text{m}, \quad (\text{A3})$$

and wet or field-aged tensile strengths of about 90–160 MPa for regenerated cellulose, 200–300 MPa for cotton, and 100–150 MPa for wool [26–31]. For an inertial-range strain rate $\dot{\gamma}_L \sim (\varepsilon_t/L^2)^{1/3}$, the peak bending stress of a slender fiber is estimated as

$$\sigma_{\max} \simeq \frac{8}{3\pi} \frac{\zeta_{\perp}(L) \dot{\gamma}_L L^3}{d^3}, \quad \zeta_{\perp}(L) \simeq \frac{4\pi\mu_w}{\ln(2L/d) + 0.5}, \quad (\text{A4})$$

TABLE 1. Inertial-range breakage length L_{brk} for $d = 16.7 \mu\text{m}$ fibers under the ACE turbulence brackets. Thresholds rescale approximately as $d^{9/7}$.

Fiber class	L_{brk} (Surface)	L_{brk} (5 m)
Regenerated cellulose	$\sim 9\text{--}15$ cm	$\sim 15\text{--}25$ cm
Cotton	$\sim 13\text{--}20$ cm	$\sim 21\text{--}33$ cm
Wool	$\sim 10\text{--}15$ cm	$\sim 16\text{--}24$ cm

where μ_w is the dynamic viscosity of seawater and $\zeta_{\perp}$ is the perpendicular slender-body drag coefficient [32]. Setting $\sigma_{\text{max}} = \sigma_{\text{mat}}$ gives the breakage length L_{brk} [20]. The resulting ACE brackets are shown in Table 1.

Thus, L_{brk} is centimetric and much larger than both η and the fitted range $L \lesssim 1$ mm. The submillimeter fibers considered in the main text are therefore below the turbulence-limited breakage threshold, so their SML dynamics can be treated as attachment-detachment exchange rather than active interfacial fragmentation.

APPENDIX B: LENGTH-FLAT SUBCUTOFF SOURCE FROM EQUIPROBABLE SCISSION

This Appendix justifies the approximately length-independent source S_0 used in the main text. At a fixed depth z^* , write $c^*(L, t) \equiv c(z^*, L, t)$. A standard fragmentation balance is

$$\partial_t c^*(L, t) = \int_L^\infty h(P) c^*(P, t) B(L|P) dP - h(L) c^*(L, t) + S_{\text{ext}}(L, t) - R_{\text{ext}}(L, t), \quad (\text{B1})$$

where h is the breakage rate, $B(L|P)$ is the daughter-length kernel, and S_{ext} and R_{ext} collect nonfragmentative sources and removals. Fragmentation arrests below the breakage cutoff,

$$h(L) = 0, \quad 0 < L < L_{\text{brk}}, \quad (\text{B2})$$

with L_{brk} centimetric under ACE conditions (Appendix A). For a breaking parent of length $P \geq L_{\text{brk}}$, binary equiprobable scission gives the uniform daughter kernel

$$B(L|P) = \frac{2}{P} \mathbf{1}_{(0,P)}(L), \quad P \geq L_{\text{brk}}, \quad (\text{B3})$$

where the factor 2 counts both daughters. Defining the parent breakage flux as

$$J(P, t) \equiv h(P) c^*(P, t), \quad (\text{B4})$$

the gain term for any subcutoff length $0 < L < L_{\text{brk}}$ becomes

$$\begin{aligned} S_{\text{in}}(L, t) &= \int_{L_{\text{brk}}}^\infty J(P, t) B(L|P) dP \\ &= \int_{L_{\text{brk}}}^\infty \frac{2J(P, t)}{P} dP \\ &\equiv S_0^{\text{frag}}(t), \quad 0 < L < L_{\text{brk}}. \end{aligned} \quad (\text{B5})$$

Thus, the fragmentation input is independent of daughter length throughout the subcutoff interval. Since the analyzed fibers satisfy $L \lesssim 1$ mm $\ll L_{\text{brk}}$, this yields

$$S_{\text{in}}(L, t) \simeq S_0^{\text{frag}}(t), \quad L \lesssim 1 \text{ mm}. \quad (\text{B6})$$

In quasisteady conditions S_0^{frag} can be absorbed into the effective S_0 of the column model, together with any other approximately length-flat contribution. Therefore, the observed increase of the surface spectrum with L over the fitted window must be attributed to retention/removal, not to a length-increasing production term.

APPENDIX C: MIXED-LAYER SCALING UNDER ACE CONDITIONS

This Appendix gives the scale estimates supporting the nearly well-mixed approximation $c(0, L) \simeq c(H, L)$ and the weak length dependence of the bulk removal kernel $k(L)$ over the ACE submillimeter window. To match the constant- K closure used in the main text, we estimate the representative diffusivity over $0 < z \leq H$ by evaluating a mixing-length form at $z = H/2$:

$$K \equiv \kappa u_{*w} \frac{H}{2} \simeq 9 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}, \quad H = 5 \text{ m}. \quad (\text{C1})$$

The corresponding mixing time across the sampled layer is

$$t_{\text{mix}} \sim \frac{H^2}{K} \simeq 2.8 \times 10^3 \text{ s} \simeq 0.8 \text{ h}. \quad (\text{C2})$$

For an isolated slender fiber, balancing buoyant weight per unit length with viscous drag gives

$$w_s(L) = \frac{\Delta \rho g \pi d^2 / 4}{\zeta_{\perp}(L)} \simeq \frac{\Delta \rho g d^2}{16 \mu_w} \left[\ln \left(\frac{2L}{d} \right) + 0.5 \right], \quad (\text{C3})$$

where $w_s > 0$ is downward and $\Delta \rho = \rho_{\text{mat}} - \rho_w$. Using Eq. (A3) and a conservative cold-seawater viscosity $\mu_w = 1.5 \times 10^{-3} \text{ Pa s}$ gives

$$\begin{aligned} |w_s(L)| &\sim 10^{-4} \text{ to } 3 \times 10^{-4} \text{ m s}^{-1}, \\ \frac{H}{|w_s|} &\sim 5\text{--}12 \text{ h} \end{aligned} \quad (\text{C4})$$

for the dominant ACE fiber classes and $L = 200\text{--}600 \mu\text{m}$. The associated Péclet number is

$$\text{Pe}(L) \equiv \frac{|w_s(L)|H}{K} \simeq 0.07\text{--}0.15, \quad L = 200\text{--}600 \mu\text{m}, \quad (\text{C5})$$

so turbulent diffusion dominates over settling or rising across the top H meters.

A useful benchmark for bulk removal is the rate required to localize a boundary forcing within a layer much thinner than H :

$$k_{\text{crit}} \equiv \frac{K}{H^2} \simeq 3.6 \times 10^{-4} \text{ s}^{-1}, \quad (\text{C6})$$

corresponding to a subhourly timescale. The direct drift-based reference rate is instead

$$k_{\text{ref}}(L) \equiv \frac{|w_s(L)|}{H} \sim (2\text{--}6) \times 10^{-5} \text{ s}^{-1}, \quad (\text{C7})$$

which is already several times smaller than k_{crit} . The Damköhler number for the main-text column model is

$$\text{Da}(L) \equiv \frac{k(L)H^2}{K}, \quad (\text{C8})$$

and the drift-based reference value is

$$\text{Da}_{\text{ref}}(L) \equiv \frac{k_{\text{ref}}(L)H^2}{K} = \frac{|w_s(L)|H}{K} \equiv \text{Pe}(L) \simeq 0.07\text{--}0.15. \quad (\text{C9})$$

Additional open-ocean bulk losses such as aggregation or biofouling-driven export need not be identical to k_{ref} , but they are not expected to act on sub-hourly timescales in dilute conditions. Hence, $\text{Pe} \ll 1$ and $\text{Da} \lesssim O(1)$, with the

ACE-based reference value well below unity, support the leading approximation used in Eq. (15).

Finally, Eq. (C3) shows that the most direct advective contribution $|w_s|/H$ depends on length only through a logarithm. Over the fitted window,

$$\frac{|w_s(600 \text{ } \mu\text{m})|}{|w_s(200 \text{ } \mu\text{m})|} \simeq \frac{\ln(2 \times 600/d) + 0.5}{\ln(2 \times 200/d) + 0.5} \approx 1.3, \quad (\text{C10})$$

with d in micrometers in the numerical ratio. Combined with Appendix A, which excludes submillimeter turbulent breakage as a strong sink, this justifies treating $k(L)$ as weakly length dependent across $L \simeq 10^2\text{--}10^3 \text{ } \mu\text{m}$.

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