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Accumulation and Transformation of Microplastics in Estuarine Fronts

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Abstract

Million tons of riverine plastic waste, numerically dominated by microplastics, annually enter the ocean via estuaries. Featured by strong horizontal convergence, estuarine fronts, ubiquitous coastal features, plausibly accumulate, transform and further involve microplastics into diverse processes, but have received limited attention. In this Perspective, we discuss the accumulation potential of microplastics and its subsequent interactions with physical-biological-geochemical processes at estuarine fronts. Microplastics fragmentation and transformation could be enhanced within frontal systems due to strong turbulence and interactions with sediment and biological particles, thus intensifying potential impacts on ecological and biogeochemical processes. The concurrent accumulation of microplastics and biota at fronts provides a unique chance to assess microplastics risks at high concentrations, a likely common scenario in future ocean. Transdisciplinary efforts in the mechanics of plastic dispersal, accumulation and fate in frontal zones will advance the knowledge of riverine microplastics fate, favoring the developments of mitigation policies, strategies and techniques.

Introduction

In 2016, an estimated 19–23 million metric tons (MT) of land-based mismanaged plastic waste entered aquatic ecosystems worldwide[1]. In the environment, plastic debris break into smaller pieces termed microplastics (<5 mm) via natural fragmentation processes[2]. Microplastics, coming in different sizes, shapes, colors and chemical matrices[3], dominate the number of plastic debris and represent a planetary threat to Earth system[4]. As plastic load into natural environments will raise in next few decades[5], their continuous fragmentation will inevitably lead to an elevated exposure of aquatic organisms to microplastics and associated chemicals. It was projected that 91% of mismanaged plastic waste generated globally was transported via watersheds (>100 km^2, suggesting rivers as major pathways for plastics to the ocean[6]. A critical estimate of the annual riverine plastic loads into the global ocean is 0.8 to 2.7 million MT[7], roughly representing up to 50% of land-based plastic emissions (4.8–12.7 million MT)[8].

Upon reaching estuaries, microplastics, like well-studied suspended particles, are fractionated by physical, geochemical, biological, and ecological processes, and these dynamics potentially determine the fate of plastics[9-11]. One important hydrological feature in estuarine system is the formation of density fronts when two distinct water masses interact and present sharp density transitions[12,13]. In general, density fronts occur throughout the ocean at different spatial and temporal scales and are generally active in that there are a convergent flow and vertical circulations[12,14-16]. Their most immediate environmental effect is the occurrence of poor water quality due to the frontal circulation converging flotsam, toxins, and organisms[17-20]. Frontal accumulation of pollutants is of functional importance in the dispersion of oceanic pollutants. For instance, the enhanced aggregation of surface drifters by fronts in the Gulf of Mexico indicates that the convergence associated with fronts is efficient in accumulating floating pollutants, thereby possibly facilitating cleanup[21]. Compared to the submesoscale fronts in the open ocean, estuarine fronts usually exhibit considerably stronger horizontal convergence[22-24], vertical velocities[25,26], and turbulent mixing[27-29] (FIG. 1), plausibly resulting in stronger convergences of flotsam and various types of organisms[30,31]. These, in turn, have major implications for the biological, ecological, and biogeochemical health of the estuarine ecosystem[13,32]. Although some observations suggest that estuarine fronts have potential influences on the redistribution and fate of riverine plastics[31,33-35], these impacts, especially on microplastics, have not yet received sufficient attention[36-38].

The aim of this Perspective is to illustrate the potential effects of estuarine surface fronts on the accumulation, transformation and transportation of microplastics by combining insights from hydrology, biology, ecology and geochemistry. We also propose that plastic hotspots at estuarine fronts provide opportunities for the development and mobilization of mitigation strategies and collection technologies to offset riverine plastic emissions, complementing existing approaches. Finally, we suggest knowledge gaps that shall be addressed in future work to develop a better mechanistic understanding of how microplastics behave in estuarine frontal systems.

Main types of estuarine fronts

Due to the interaction between buoyant freshwater and dense seawater, estuaries exhibit large salinity variance and the strongest density fronts of any marine environment[12,39]. Estuarine surface fronts have apparent surface features allowing for easy observations of pollutant accumulation[13,40];

therefore, this type of fronts is emphasized in this perspective. Bottom fronts are not discussed here since they are not as easily observed as the surface fronts. However, they also have potentially important effects on riverine plastics[35,41].

Three most common surface fronts in estuarine systems are considered: shear fronts, tidal intrusion fronts and plume fronts (FIG. 2). These types of fronts are not mutually independent. For instance, shear fronts can produce buoyancy-driven flow structures that propagate away from the generation region as plume fronts[12].

Shear fronts. As one kind of the most common fronts inside the estuary[40], shear fronts are usually aligned longitudinally and located at the inner edge of the shoals[42], over the main channel[43] or behind headlands and islands[44] (FIG. 2a). They might extend for several kilometers and exist for several hours in one tidal cycle. Shear fronts are often triggered by the cross-channel shear of surface longitudinal tidal currents in the regions with sharp depth gradients or behind headlands and islands, and develop through flow convergences[24,44] (FIG. 2a,b). The well-known axial convergence front is one particular case of shear fronts because it is triggered by the transverse shear of tidal currents[43]. Although termed as “shear front”, some other mechanisms might also contribute to the frontogenesis, such as confluence[45], convergence[24] and heterogeneous cross-channel distribution of tidal mixing[46].

Tidal intrusion fronts. Tidal intrusion fronts are often formed when denser coastal waters plunge beneath lighter estuarine waters during a flood tide into the constricted estuary mouth[47] (FIG. 2a,c). Intrusion fronts will be evident in estuaries where incoming tidal water masses prevail over river discharge. They are particularly pervasive in small estuaries around the world and usually marked by a pronounced ‘V’ shape[48] (FIG. 2a). In addition to the estuarine mouth, tidal intrusion fronts can also occur when tidal currents flow across constricted topographies inside the estuary[49].

Plume fronts. A river plume is formed when freshwater of riverine origin spreads over the coastal water. As the plume spreads offshore, it creates one or several clear frontal boundaries onto the continental shelf between the river plume and neighboring marine waters (FIG. 2a,d). These boundaries with high horizontal density gradients are termed as plume fronts (FIG. 2d). The locations of plume fronts vary in different estuarine systems, which mainly depend on the extension and pathway of the diluted water as well as some local frontogenetic mechanisms[50]. The triggering mechanisms for the plume frontogenesis include the flow separation at the jetty of the estuarine mouth due to cross flow[51], hydraulic response to flow over the shoal[50], the seaward advection of the tidal intrusion front[13], and the interactions between the coastal and plume currents[16].

Overall, all three types of fronts usually exhibit strong surface convergence, downwelling and turbulence (FIG. 1). In a realistic front, frontogenesis is the result of several mechanisms rather than just one. Despite complex dynamics, the three types of surface fronts are often visually observable as well as detectable through satellite images due to watercolor differences and accumulations of foam and debris (FIG. 2b,c,d). Since their occurrence is related to periodical tidal currents and topographies, their approximate occurrence locations and times in an estuary are predictable from the observations of river discharge, tidal currents, and topography. The prediction of a more precise occurrence time and location of estuarine fronts often requires high-resolution numerical modellings[16,52,53], because aperiodic forcings, such as river discharge and winds can influence the generation and movement of some fronts.

Microplastic accumulation

Various frontal processes spanning from the coast to the open ocean are thought able to cause surface convergence, trap and retain plastic debris[54-56]. By converging plastic debris, fronts might offer an opportunity for focused cleanup actions in the ocean[55,57]. The differences in microplastics abundances between open-ocean frontal and ambient waters demonstrate the marked convergence effects along the fronts (meso[58] and submeso-scale[59-61]) (FIG. 1b). Despite this fact, convergent features accumulating floating plastics are rarely studied in the open ocean[55], and the investigation of estuarine fronts on retaining plastics is even fewer. Nevertheless, the existing studies clearly identify the enrichment of microplastics at fronts compared to ambient waters[36-38] (FIG. 1b). Meanwhile, we must note that microplastics abundances (300-5000 μm; 89-2200 pieces/m^3) at estuarine fronts, standardized with methods in literature[62,63], are remarkedly higher than those (1.4-123.2 pieces/m^3) observed in the open-ocean fronts, and larger than the maximum value observed within the Great Pacific Garbage Patch (9.0 pieces/m^3; FIG. 1b)[64], believed to hold the greatest concentration of floating plastics of all ocean gyres[65]. Modelling studies also demonstrated the occurrence of microplastics hotspots along salinity fronts[66,67]. Additionally, some other studies ascribed the observed distribution patterns of microplastics to the estuarine salinity fronts[31,33,34]. All these preliminary evidences strongly suggest that estuarine fronts, as transition zones between the input sources of land-based plastic debris and the open ocean have the capacity to accumulate extraordinarily high loads of plastics. Compared to the inner shelf and open-ocean fronts, the recurrent estuarine fronts establish more rapidly and are predicted with confidence in time and space[19]. Furthermore, estuarine fronts are geographically and temporally accessible and are easily recognized by environmental practitioners with a trained eye because of the accumulation of foam and flotsam and the contrasting watercolor and clarity (FIG. 2). The recurrent and cumulative features of estuarine fronts are important to retain riverine floating materials, and consequently highlight their central role in intercepting and accumulating plastic debris. Although not detailed in this context, we must note that the estuarine bottom fronts are also efficient in trapping and concentrating riverine macro-plastic debris[35,41].

Microplastic transformation

Due to the characteristic flow convergence, floating materials are retained at fronts where the matching of physical, biological and geochemical time-space scales provides the potential to greatly modify the properties of suspended materials from rivers to the ocean[48,68] (FIG. 3). Microplastics incubated in this complex reactor can be subject to major alternations (fragmentation and aggregation, FIG. 3b,c,d), largely determining their environmental fate and effects.

Fragmentation. In the natural environment, plastics become brittle and fragment into smaller pieces under different weathering processes including photodegradation, biodegradation, thermal degradation, mechanical destruction and hydrolysis, of which photodegradation is the only notable mechanism leading to rapid environmental degradation of plastic polymers[2]. Exposure of plastic to ultraviolet (UV) radiation is the critical step to initiate autocatalytic thermal oxidation that principally accounts for their subsequent fragmentation[69]. Once initiated, oxidation reactions could result in the bulk fragmentation of plastics yielding large daughter fragments; at the same time, the surface-ablation fragmentation of plastics, which releases large amounts of microscale plastics from UV-facilitated brittle surface layer, will progress along with the bulk fragmentation. The mechanical forces such as sand grinding, collision and interaction with biotic particles, wave and wind actions, can disintegrate and detach the weathered surface layer into micro- and nanoplastics through the abrasion wear[69,70]. Both field and laboratory data indicated that the surface-ablative fragmentation is primarily responsible for most of secondary microplastics in the environment[71-75]. In rivers and estuaries, microplastics at different states of degradation were widely identified, manifested by obvious rough surface textures (for instance, pits, fractures and flakes) and discoloration[76-79]. The wear of photo-oxidated plastics against erosive sand can efficiently generate smaller fragments, likely dominated by particles smaller than 100 μm[73]. After 500 hours of exposure in the UV light chamber, polypropylene plastics incubated in seawater showed strong degradation (cracks and holes) on their surfaces with missing small pieces of material in the sub-micron range[75]. This result was attributed to the combined action of UV radiation and wave action, and the missing fragments accounted for an average 0.1% of the initial plastic weight. To better understand this surface-ablation mode of fragmentation, we calculated the theoretical amount of 100 nm and 1 μm cubic particles generated from the weight loss of polypropylene plastics in REF[75]. The 0.1% of weight loss approximately equals to 10^{18} and 10^9 pieces of 100 nm and 1 μm particles, respectively, corresponding to 2×10^{16} pieces/liter and 2×10^7 pieces/liter. These large numbers of secondary fragments from the surface-ablation fragmentation might represent a pressing health concern for aquatic biota. The frontal zone is well known as an effective trap of the river-laden sediments (for example, the concentration could be up to 10 g/L in the Amazon frontal zone[80]) and biological particles[12,19]. Additionally, the turbulent kinetic energy dissipation rate could be about 1–2 orders of magnitude greater along estuarine fronts than in the surrounding waters (FIG. 1a). Due to the stronger turbulent energy and higher concentrations of suspended particles at fronts with respect to ambient conditions, the encounter kernel rate (Collision Frequency) of suspended particles will substantially increase in estuarine frontal zones[81-85] (BOX 1). Therefore, the presence of single or combined factors (high concentrations of particles and strong turbulence) in the frontal zones will considerably increase the probability of the surface-ablative fragmentation of UV-weathered plastic debris (FIG. 3b). However, the surface-ablation mode of fragmentation in aquatic environments is not yet sufficiently understood[74,75,86-88], and further data are required to disclose the detailed dynamics of this process.

Aggregation. Besides the transport process facilitating particle collisions (BOX 1), destabilization with reducing interparticle repulsion also controls particle aggregation[89]. Although the destabilization mechanisms are initially assumed to cover small-sized particles (<1 μm), they also apply to the aggregation processes of millimeter-sized particles[81]. Upon entering rivers, particles are immediately coated with natural organic matter (mainly carboxyl and phenolic-OH[90]) producing a uniformly negative surface charge[10]. The negative charge on the particle-organic matter surface creates an electrostatic ‘double layer’, whose distance determines the range of interparticle repulsive forces and restricts particle aggregation[81]. As approaching the estuaries, counter ions (especially cations Ca^{2+} and Mg^{2+}) are attracted by electrostatic forces, which will screen the electrostatic repulsive force and compress the distance of the double layer. The compression of double layer allows the short-range attractive *van der Waals forces* to occur, permitting particles to approach more closely[10,81]. Due to the raising ionic strength, the enhancement of river-borne particle aggregations in estuaries has been widely acknowledged[10,91,92].

Although the charge neutralization is the major destabilization process, some other mechanisms also come into play: an example is the hydrophobic character of particles which provides appreciable attraction between particles through the so-called 'hydrophobic bonding[81]. The resulting attractive force between particles and hydrophobic segments is unexpectedly large and promotes considerable aggregation[93,94]. The hydrophobic interaction is particularly true when considering the higher hydrophobicity of plastic particles in the aquatic environment compared to naturally suspended particles.

Apart from the physical and geochemical mechanisms of particles coagulation, biologically-generated organic compounds like extracellular polymeric substances (EPS)[95], also play an important role in holding the particles together[85,96]. EPS exuded by phytoplankton and bacteria in aquatic systems is constituted of sugars, proteins, nucleic acids and lipids. EPS also serves as the biological glue which controls coagulation efficiencies and enhances the formation of particle aggregations[97,98]. The sticky nature of EPS is usually attributed to its polyanionic nature, such as carboxylic and sulfate half-ester groups[99,100]. For example, the stickiness of the diatom-derived transparent exopolymer particles (TEP), one type of EPS, was observed as generally 2–4 orders of magnitude higher than that of most other particles[101,102]. Laboratory experiments showed that biogenic particles could intensively interact with microplastics and generate more pronounced aggregates and TEP with respect to treatments without plastic addition[103-105]. Furthermore, TEP stickiness appears to increase along the salinity gradient, implying a seaward enhancement in particle aggregation[106]. The production of TEP could also be enhanced by high cell abundances[102] and high turbulence intensity[107]. These evidences indicate that the secretion of EPS by microorganisms in estuarine fronts could be particularly elevated. For instance, TEP from organisms at fronts created mucilaginous foams and gels at the water surface[108], and condensed gelatinous aggregates along frontal systems were observed in the northern Adriatic Sea[109]. Additionally, particles can be ingested by organisms and expelled in their feces or pseudo-feces[110,111]. The bio-deposits of many aquatic animals are generally mucus-bounded[112] and can trap other particles, further aggregating riverine particles[113]. These biogenic compounds determine the stability and particle size of aggregates and thus are essential to maintain the steady-state population of aggregate sizes in the presence of the turbulent forces[114]. The high abundance of organisms and biological activities, combined with the increased particle collision frequency due to turbulent forces (BOX 1) and geochemical conditions at estuarine fronts, will enhance the aggregation of microplastics (FIG. 3d).

Microplastic transport

Once plastics are entrapped in the frontal systems, transport mechanisms become more complex because numerous physical and biological processes interact as waters of different densities come into contact[19]. Considering the enhanced cross-frontal vertical circulations and biological factors, a marked three-dimensional transport of microplastics might be expected at the front.

Physical transport. Horizontally, fronts generally tend to converge materials in the cross-front direction and transport them mainly in the along-front direction[15]. Once fronts fragment or dissipate, the convergent materials (including microplastics) are likely dispersed into the surrounding waters, resulting in a single large pulse of plastic[68]. Vertically, estuarine fronts usually feature strong downwelling velocities and turbulent mixing (FIG. 1a). Results from models have clarified that strong downwelling currents and turbulence at fronts can subduct surface particles into the water column[116,117] (FIG. 3a). In combination with the enhanced aggregation, the sinking rates of microplastics in frontal zones will considerably increase, speeding up their removal from the surface. Experiments and field observations demonstrate that aggregates are an efficient vector for vertical transport of microplastics in the water column through increasing settling velocities by orders of magnitudes[105,118-120]. Lastly, smaller microplastics trapped in mucilaginous foams along the fronts might be lifted into the air by breaking waves and winds. Although studies in this respect are limited, both microplastic fragments (≤300 μm) and microfibers (up to 750 μm) have been widely detected in the wet[121-124] and dry atmospheric depositions, suggesting longer-range transport[125]. Furthermore, models and observations agree in the possible transfer of microplastics from surface seawater to atmospheric aerosols through wind and wave actions[126-128], substantially contributing to the atmospheric microplastics load. As such, 11% of atmospheric microplastics in the western United States derive from the secondary re-emission of floating plastic marine debris[128]. These evidences suggest that microplastics accumulation zones in aquatic environments represent important potential sources of atmospheric microplastics, and this particularly applies to the 3-D transport of microplastics at fronts.

Bio-transport. The elevated plankton biomass in estuarine fronts creates feeding “hotspots” for planktivorous fishes (for example anchovy, herring and juvenile salmonids), which subsequently attract piscivorous fishes, birds, and mammals and enhance the energy and pollutants transfer to higher trophic levels[129,130]. If the swimming speeds of these organisms overcome the convergent current velocity, the advection and diffusion of organisms as well as the associated pollutants are likely to occur[131]. The bio-transport of persistent organic pollutants (POPs), such as polychlorinated biphenyls and dichlorodiphenyltrichloroethane in migrating birds, marine mammals and fishes has been observed[132-134]. It is therefore expected that microplastics could experience a similar transport pattern via being mistaken by or attached to aquatic organisms in fronts (like seaward juvenile salmonids and seabirds[130,135]) (FIG. 3a).

Modelling microplastic transport. Numerical modeling is one of the most effective tools to simulate and study estuarine fronts and microplastics transport. Although the number of observations of estuarine surface fronts has massively increased since the 1970s (REFS[12,13,19,40]), numerical simulations in realistic estuaries only concentrate in the 21st century, benefiting from the increasing resolution and performance of three-dimensional baroclinic hydrodynamic models. To date, some numerical models have been applied successfully in a few estuaries to simulate frontal dynamics, including the occurrence time and locations of fronts, frontogenesis, three-dimensional velocities at fronts and frontal instabilities (Supplementary Table 1). Based on the hydrodynamic fields generated from these models, the transport and fate of microplastics in estuaries can be further simulated, and thus help predict microplastics hotspots[66,67].

Numerical simulations of the transport and fate of microplastics in the coastal and open ocean were generally carried out based on the Eulerian or Lagrangian frameworks. In the Lagrangian framework, microplastics are represented by individual virtual particles, which are allowed to move through the time-evolving velocity fields[136,137]. The effect of turbulence is sometimes included as ad hoc random motions[137,138]. In addition to the extensive applied Lagrangian particle-tracking oceanic models summarized in REF[137], some other particle-tracking models have also been applied to microplastic transport simulations in coastal and estuarine regions, for instance the three dimensional hydrodynamic and suspended sediment transport model (HYDROTAM-3D)[139], Track Marine Plastic Debris (TrackMPD)[140], Delft3D-Water Quality Particle tracking module (D-WAQ PART)[141], and Ichthyoplankton (Ichthyop)[142]. Unlike the Lagrangian approach, Eulerian models simulate microplastics as passive tracers in terms of their mass or volume concentrations, which are advected by the velocity fields and diffused by the parameterized turbulence[67].

Besides the hydrodynamic fields, which are considered in the common oceanic particle-tracking models, some other important factors also have effects on microplastics movements, such as the physical properties of plastic particles (density, shape, size), windage, beaching, sedimentation, resuspension, fragmentation, biofouling, and ingestion by animals. As an example, the difference between the densities of plastic particles and ambient waters affects the vertical movements of microplastics[143], whereas the fragmentation-facilitated decrease in particle size and biofouling influence plastic transport[144,145]. Therefore, modeling the transport trajectories of oceanic microplastics is challenging and all of the current numerical models employ certain simplifying assumptions. Two most frequently used assumptions are considering microplastics as positively buoyant particles and tracking microplastics under the effects of ocean surface currents, without including additional mechanisms of sinking, ingestion or other removal from the ocean surface. Such simplified models have been strikingly successful in explaining the hotspots of microplastics in the coastal- and open-ocean surface waters[66,146,147]. However, there is still a large gap between masses of floating plastics in the ocean and the land-based fluxes of plastic debris to the ocean, sparing discussions about "missing plastics"[8,148,149]. To better understand the final sinks of these "missing plastics", some modeling efforts have also simulated or parameterized more mechanisms, including the vertical movement due to buoyancy[143] and mixing[138], beaching and re-suspension[150,151], sedimentation[152], fragmentation[153], and biofouling[144,154].

As stated above, although the accuracies of the hydrodynamic and plastic-tracking models are waiting for future improvements, their successful applications in previous studies have shed light on microplastic dynamics at estuarine fronts. By simulating estuarine dynamics and microplastic transport, Cohan et al. (2019)[66] and Bermurdez et al. (2021)[67] found that microplastics accumulate at the fronts of the Delaware and Guadalquivir estuaries, respectively. With the development of the hydrodynamic and microplastic-tracking models, the simulations of microplastic dynamics in estuaries are worthy of efforts, especially the processes related to accumulation, redistribution and residence time at fronts.

Ecological impacts

The concurrence of pollutants and organisms at fronts through advectively-imposed matching or behavioral movement inevitably threatens the estuarine ecosystem health and biogeochemical processes[18,19]. High levels of microplastics at fronts resulting from convergent circulations are likely common in the future as the annual plastic waste entering aquatic ecosystems is expected to increase in the coming decades[5,155]. Therefore, estuarine frontal regions are key environments, where the understanding of the ecological consequences of microplastics is critical to develop ecological and biogeochemical models for future predictions.

Ecotoxicological risk. Biological enrichment at estuarine fronts is prevalent in a wide range of neuston and planktonic organisms, such as phytoplankton, planktonic copepods, fish eggs, larval fishes and insects[131,156]. The concentrated biomass coupled to high abundances of microplastics raises the probability of encounter and ingestion of microplastics for aquatic organisms in frontal zones. Gove et al. (2019)[59] found that the plastic-to-larval fish ratio (7:1) in the coastal ocean convergence along the coast of Hawaii Island was 14 times that in the ambient waters. Moreover, they identified that plastic ingestion by larval fishes in the oceanic fronts was 2.3-fold higher than in ambient waters. Compared to adult fishes, larval fishes were more vulnerable to the consequence of microplastics ingestion because of their underdeveloped organs[157]. A wide range of aquatic organisms at the bottom of the food chain can ingest microplastics[158,159], showing a positive correlation between the bio-uptake rates and microplastics abundances[160,161]. Microplastics can substitute the food in the diets of zooplankton and thus decrease their natural food consumption, subsequently lowering the carbon export efficiency through an impaired fecal pellet sinking rates and the biological pump[120,162]. Smaller microparticles (<150 µm) can translocate across biological membranes and become entrapped in organisms' tissues, potentially leading to bioaccumulation and biomagnification through the entire food web[4,163]. Small sized particles can also accelerate the release of chemicals inherent in plastic polymers (for instance, carbon and additives)[164]. Some contrasting evidences exist as well: one research in the Cooper River, USA found no statistically significant differences in microplastic consumption by zooplankton at the tidal fronts and in the surrounding waters, although higher abundances of microplastics were identified at the front[36]. Low grazing rates of microplastics by zooplankton were also observed in laboratory assays that typically employ higher plastic concentrations[165,166], which was largely ascribed to the animal selective feeding behavior. Altogether, these findings suggest that microplastics consumption is a function of plastic abundances as well as size and shape, while other factors related to plastics (such as biofouling, aggregation, chemical sorption and release), and the aquatic biota feeding mechanisms, also play a key role[167-170]. In frontal systems, the synergic effects of high particles abundances, small particle size, enhanced plastic incorporation into biological aggregates expectedly increase microplastics bioavailability. This higher bioavailability can enhance the accessibility of smaller microplastics to biological tissues, accelerate additive leaching rates, and consequently expose different trophic organisms in frontal habitats to the threats of plastic pollution[4]. The shorter and more efficient path length of food webs in frontal systems[171] has a great potential to rapidly channel a sufficient proportion of ingested microplastics to higher trophic levels. Besides resulting in the elevated ratio of microplastic-to-prey particles, the convergence of both plastic and biological particles at fronts also has the potential to dilute the concentrations of microplastics, hence making microplastic bioavailability become more difficult to model and deserving further attention, since microplastic dilution in frontal systems has not been verified yet.

Biogeochemical influences. Aside from increased ecotoxicological threats through microplastics ingestion, the accumulation of these particles at fronts can also impose substantial impacts on biogeochemical elements' cycling. Enhanced particle fragmentation and strong turbulence in frontal regions, as well as photo-oxidation, can increase the leaching rate of plastic-related chemicals through the deterioration and disruption of polymeric structures[164,172]. The leaching rate of one-half additives from a plastic fragment increases exponentially with a decrease in size[164]. Under controlled turbulent conditions, leaching rates of additives and polymer oligomers from microplastics are considerably enhanced. In these settings, the rate of chemical release from microplastics in turbulent conditions can be up to 190-fold higher than that from plastics in the non-turbulent conditions[172]. Therefore, the leaching of both fossil-based carbon in the polymer backbone[173,174] and chemical additives (at least 906 different types[175]) could be speeded up in estuarine frontal environments. Controlled experiments documented that microplastic leachates apparently changed the microbial communities and nitrogen cycling processes by transforming metabolic intermediates and enzymes activities of microbes[176,177]. Furthermore, the enhanced microplastics ingestion in frontal systems could potentially change the water biogeochemistry. It was predicted that consumption of microplastics by zooplankton in the open ocean could reduce the grazing on phytoplankton and thus result in the elevated organic carbon export, which upon remineralization decreases the oxygen and returns nutrients to the water column[178]. Zobell (1943) found that trace nutrients could concentrate on solid surfaces in the water column, thereby becoming more bioavailable and stimulating bacterial respiration[179]. Elevated nutrients on plastic surface can strengthen the metabolism and interactions of both autotrophic and heterotrophic bacteria and enhance the production of EPS and the formation of particulate aggregates[104,180]. Similar to what has been proposed for the open ocean[178], predictably increased consumption of microplastics by zooplankton might also accelerating deoxygenation of these environments[178]. In shallow estuarine systems, a rapid aggregation and consequent sedimentation of microplastics embedded into biogenic material can enhance benthic oxygen respiration creating anoxic sediments conditions; this process can have large impacts on coastal nutrient cycling and large-scale geochemical dynamics that involve chemical exchanges at the interface between seawater and sediments.

Implications for pollution mitigation

Based on a high-resolution global map showing the probability for land-based plastics to enter the ocean, Meijer et al. (2021) predicted an annual flux of riverine plastic ranging from 0.8 to 2.7 MT[7]. Contrary to previous estimates, those reported a few large rivers (47 and 5 rivers[181,182]) holding responsible for the vast majority of annual plastic load to the ocean, the results by Meijer and colleagues showed that 1656 rivers accounted for 80% of the global plastic emissions. Of these 1656 rivers, small and medium-sized rivers contributed 96% of the plastic load, whereas large rivers made up only 4.0%. The urban rivers in South East Asia and West Africa were identified as the principal contributors[7]. Understanding the mechanisms behind the transport and transformation of plastics in estuaries is a prerequisite to inform environmental stakeholders and policy makers, and for developing efficient solutions at or near the source of these debris before they reach the oceanic environment. However, progress-based observations of plastics in rivers and estuaries are still few[183,184]. Furthermore, there is an uneven distribution of studies on the world's estuarine fronts and the rivers presumably responsible for the majority of the plastic load into the world's ocean[7]. To date, knowledge on estuarine fronts is mostly derived from studies in North America and Europe, where rivers' contribution to the global plastic export is limited (FIG. 4). Contrastingly, estuarine fronts are largely understudied in Asia, where rivers account for the majority (>60%) of the total flux of plastic debris into the ocean[7]. This mismatch impedes an efficient control and mitigation of plastic pollution at these predicted hotspots, and indicates that international collaboration and common agreements on plastic management are required[185]. Despite cross-border research on estuaries in Asia is still limited, it is encouraging to note that some internal groups (for instance, the Ocean Cleanup and 'The National Geographic Society's Sea to Source: Ganges Expedition') have started to study riverine plastics in these hotspots[186-190]. In light of the substantial influence of estuarine fronts on riverine plastics, the hydrodynamics, biological and geochemical processes at fronts merit in-depth investigation when monitoring plastic pollution.

Simultaneously, lots of technologies such as net-based sampling, remote sensing, and camera technologies have been developed to monitor and reduce plastic waste in global rivers[183]. With respect to riverine plastic cleanup, the implantation of different infrastructures in river channels to extract plastic appear to be the most efficient approaches. For instance, floating booms (n=26) were employed to collect debris in the Seine River in France[191]. In 2014, a trash interceptor driven by the combination of solar and hydro power, known as Mr. Trash Wheel, was installed in the Jones Falls[192] (Maryland, USA) and has collected over 2000 tons of debris as of May 2022. By employing a similar technique, the Ocean Cleanup advocated to tackle these 1000 most polluting rivers. Estuarine fronts, as natural barriers for floating materials, can play a complementary role in intercepting plastics in all size fractions before making their way into the ocean. The main types of surface fronts are temporally recurrent, and easily predictable in time and space by making use of available data of river discharge, tidal currents, topography and perfectioned by numerical models. In the field, these fronts often show pronounced differences in watercolor, accumulations of foam and debris (FIG. 2), and enhanced surface roughness which can be detected by ship-mounted radars[193]. Therefore, recovering plastics along estuarine fronts can be reasonably practical and provide a complementary way to the currently available cleanup strategies, which can be more efficient by coupling the newly affordable collection techniques such as unmanned aerial vehicles (UAVs[187,194,195]). For example, a specifically designed UAVs, automatically locating the recurrent estuarine frontal zones, can be promising to leverage the plastic convergence at fronts and achieve considerable recovery of plastic debris. Additionally, it must be noted that estuarine fronts are regions of high ecological significance, where animals (adults and larvae) concentrate for spawning, feeding and nursing[196]. Sustainable strategies that minimally disturb ecosystems' functioning are required to mitigate plastic pollution in frontal zones. As suggested in Sherman and van Sebille (2016)[197], models that predict the dynamics of both plastics and marine life in frontal systems, should be considered to guide the development and operation of clean-up techniques and devices.

Summary and future perspectives. As the demand of plastic products increases, the riverine plastic flux to the sea will likely follow this increasing pattern in the future[1,155]. Despite substantial progress in studying transport pathways and consequences of riverine plastics moving towards the ocean, and in developing mitigation strategies and technological advancements[183], we still have a vague understanding of most processes involving microplastics in estuarine fronts. Due to the hydrodynamic, geochemical and biological characteristics of these estuarine fronts, we believe that there is a reasonable scientific confidence that frontal systems could have considerable influences on plastic transport, fate, and potential ecosystem impacts. The analysis in this perspective suggests that microplastics and other particles could converge at estuarine fronts (FIG. 1 and FIG. 3ab), leading to an enhanced plastic fragmentation as well as leaching rate of chemicals (FIG.3b and BOX 1). Furthermore, the concurrence of both microplastics and biotic particles (phytoplankton, bacteria and TEP; FIG. 3b), would increase aggregates formation rates. Microplastics transformations (fragmentation and aggregation) by frontal processes, together with environmental (circulations and air-sea interactions) and ecological factors (bio-ingestion and trophic transfer) ultimately facilitate the transport of microplastics and their integration into the food web, posing physical and chemical threats to estuarine and coastal ecosystems. The recurrent and predictable fronts in estuaries provide unique opportunities to mitigate riverine plastic pollution and prevent plastic from reaching the ocean. We also suggest that estuarine fronts, where high abundances of microplastics are similar to those expected in future ocean conditions (FIG.

1b), can be regarded as a natural laboratory setting to achieve a better understanding of future microplastics impacts on marine ecosystem, providing the opportunity to act in time. Considering the mismatch of the current knowledge on estuarine fronts and global riverine plastic emissions (FIG. 4), new research efforts should converge different disciplines to investigate microplastics in estuarine frontal zones and clarify their dispersal, fate and multifaceted interactions, aiding in developing mitigation policies, techniques and strategies. Previous studies have individuated essential research directions, crucial to a comprehensive understanding of the role of estuarine fronts in plastic pollution, such as the prediction of plastic transport trajectories in the river-estuary-sea continuum[198,199], plastic fragmentation[183], ecotoxicological effects (especially in larvae)[59], and data standardization and sharing[62,63]. Moreover, specific research topics that should be prioritized also include the observation and accurate prediction of estuarine fronts (locations, occurrence time and intensity), the converging capacity and turnover time of plastic debris in different estuarine fronts, as well as the development of pollution mitigation strategies on the basis of the hydrodynamic and biological characteristics of targeted environments. These actions we propose herein are not exhaustive and many challenges still exist due to the extremely complexity in both plastic debris composition and transformations, and estuarine processes. Nevertheless, we hope that this paper contributes to raise worldwide attention on interactions between plastic debris and physical-biological-geochemical mechanisms in frontal systems, and hopefully enables further collaborative, interdisciplinary, and international efforts to limit plastic influx to the ocean and to fill current knowledge gaps on wide-range environmental impacts of plastics.

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Author contributions S.Z was instrumental in initiating this paper. T.W. and S.Z co-led the design and writing of the article and contributed equally to this article. All co-authors provided input on the manuscript text, figures and discussion of scientific content. In particular, T.W., J.C.M. and W.J. contributed to the physical aspects of fronts. L.Z., L.G., R.M.A., R.N. M.C. and S.Z. contributed to the rest aspects. The work of T.W. and S.Z. brought the paper to its final form.

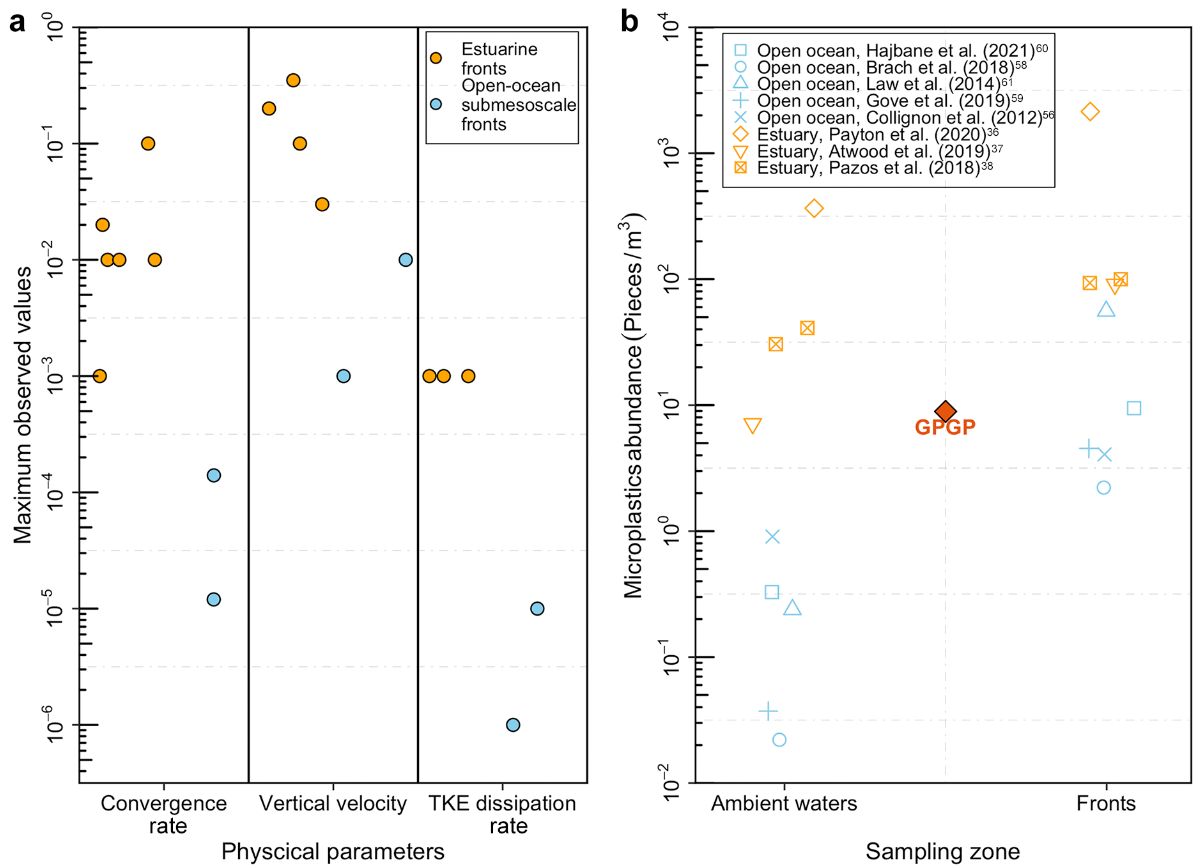

Fig.1 | Comparisons of characteristics between estuarine fronts and open-ocean fronts. a | Physical characteristics of estuarine fronts and open-ocean submesoscale fronts. The convergence rate (s^{-1})[21,22,23,24, 27,53,193,200,201], vertical velocity ($m \cdot s^{-1}$)[21,22,23,25,26,202], and turbulent kinetic energy (TKE) dissipation rate ($m^2 \cdot s^{-3}$)[22,26,27,28,29,193], are key physical factors that have important effects on the accumulation, sinking and collisions of microplastics. **b |** To assess the accumulation effects of frontal processes on floating microplastics in the estuaries and open ocean, published studies reporting microplastic abundances from both frontal zones and ambient waters were reviewed. According to the methods in literature[62,63], all these data were standardized to obtain the particle count per unit water volume (pieces/m^3) in size range of 300-5000 μm. Both estuarine fronts (orange dots)[36-38] and open-ocean fronts (blue dots)[56,58-61] result in higher abundances of microplastics in contrast to ambient waters. Microplastics in estuarine fronts are one or more orders of magnitude larger than the maximum value of microplastics in the Great Pacific Garbage Patch (GPGP, the red diamond)[64].

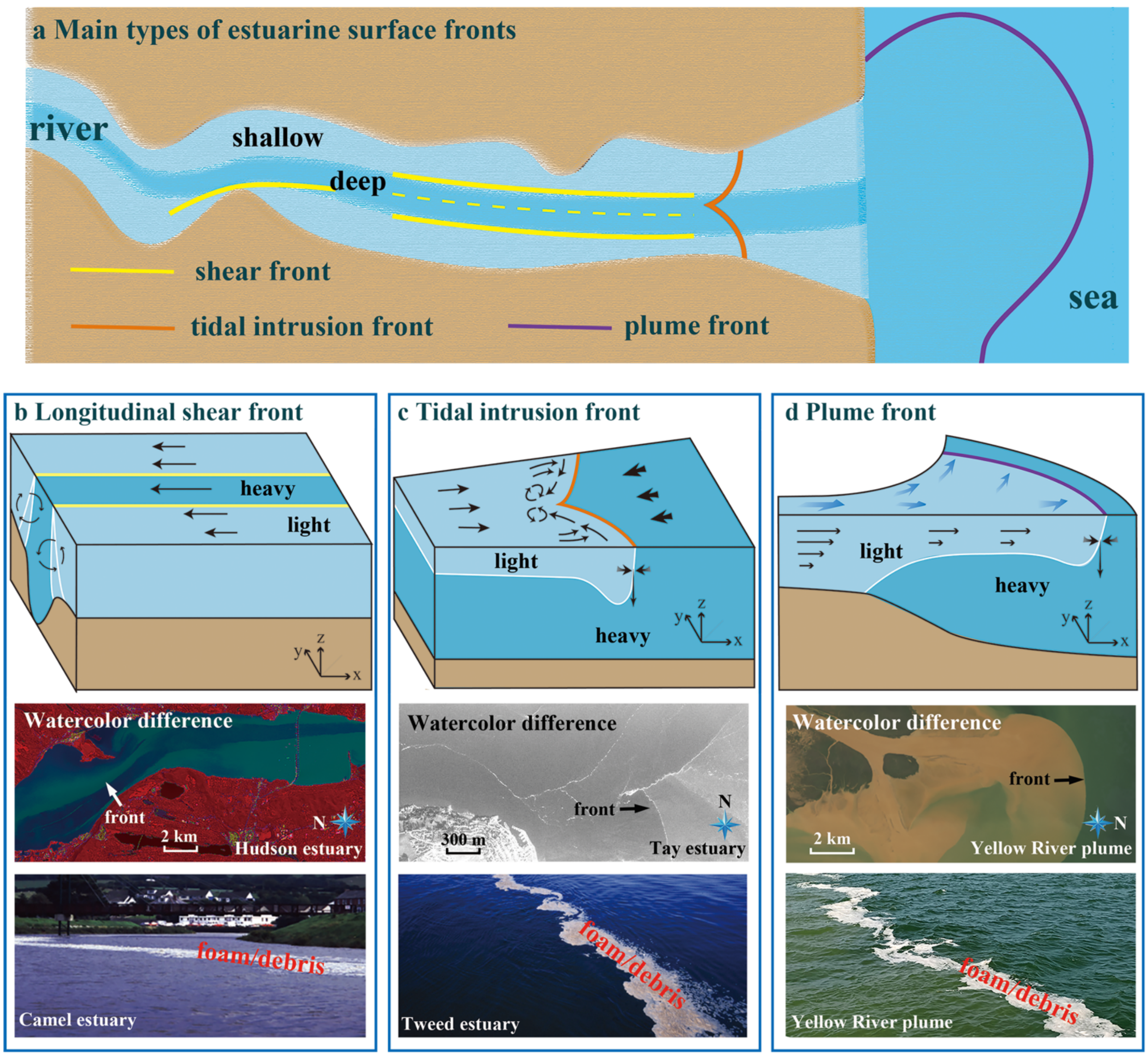

Fig.2 | Schematic diagrams of the main types of estuarine surface fronts and some examples that show their features of apparent watercolor difference and accumulation of foam and

debris. a | Schematic diagram of the locations where the three types of estuarine fronts preferably occur. **b |** Longitudinal front induced by the transverse shear of tidal velocity. **c |** Tidal intrusion front formed when denser coastal waters plunge beneath lighter estuarine waters during a flood tide. **d |** Plume front formed when riverine freshwater of riverine origin spreads over the coastal water. Watercolor images of the Hudson estuary and Yellow River plume are obtained from the Landsat satellite. Watercolor image of the Tay estuary is adapted from REF[203]. Photograph of the foam and debris lines in the Yellow River plume is taken by Tao Wang in August, 2021. Photographs of the foam and debris lines in the Camel estuary and Tweed estuary are adapted from REF[13].

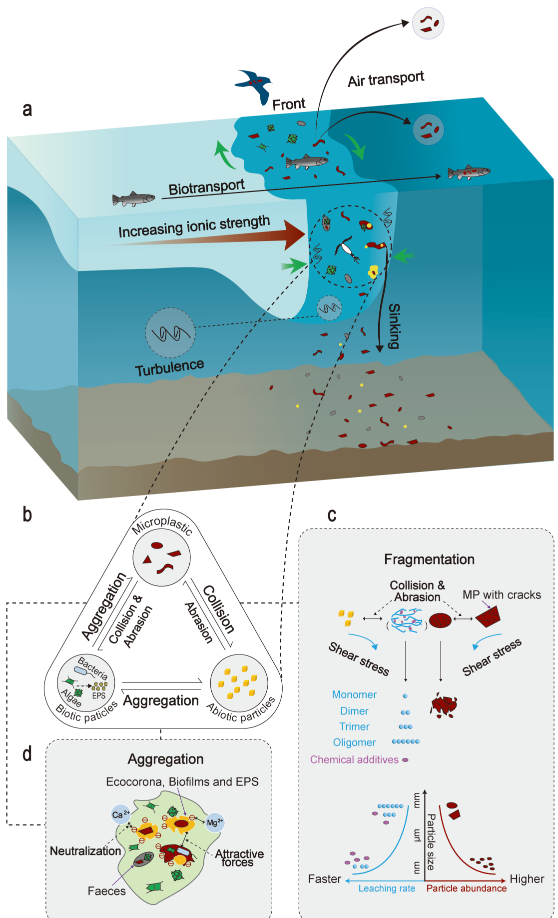

FIG | 3 Transport and transformation of microplastics in the frontal zone. a | The concurrent accumulation of organisms and microplastics due to the combination of passive convergent transport and bio-behavioral movement in response to frontal structures[19]. The convergence of phytoplankton biomass ultimately attracts animals of higher trophic levels. These animals interact with microplastics and subsequently lead to plastic redistribution. Microplastics and fibers trapped in mucilaginous foams along the fronts could be lofted into the air by breaking waves and winds, which facilitate microplastics atmospheric transport[123,126-128]. The strong downwelling currents and turbulence at fronts are able to subduct microplastics into the water column[116,117]. **b |** Interactions between microplastics and other particles (both biotic and abiotic particles) in frontal systems. **c |**

The processes of microplastic fragmentation. The enhanced collision frequency of particles in frontal systems results in the accelerated disintegration of microplastics through the detachment mechanism[84]. Simultaneously, the leaching of plastic-derived carbon (for example, monomer, trimer and oligomer) and chemical additives could also be enhanced by plastic fragmentation and strong turbulence occurring at fronts[164,172]. The abundances of secondary microplastics and leaching rates of chemicals increase exponentially with the decrease of particle size[164]. **d |** Microplastics aggregation with non-living and living particles at fronts. Besides the increased collision rates that bring particles together (BOX 1), the increased cations toward the sea[11,89] and the hydrophobicity of plastic particles[81] facilitate the attractions between particles. Additionally, the expectedly high concentrations of extracellular polymeric substances (EPS) exuded by the microorganisms, can glue these particles together and enhance aggregation[98,103,105].

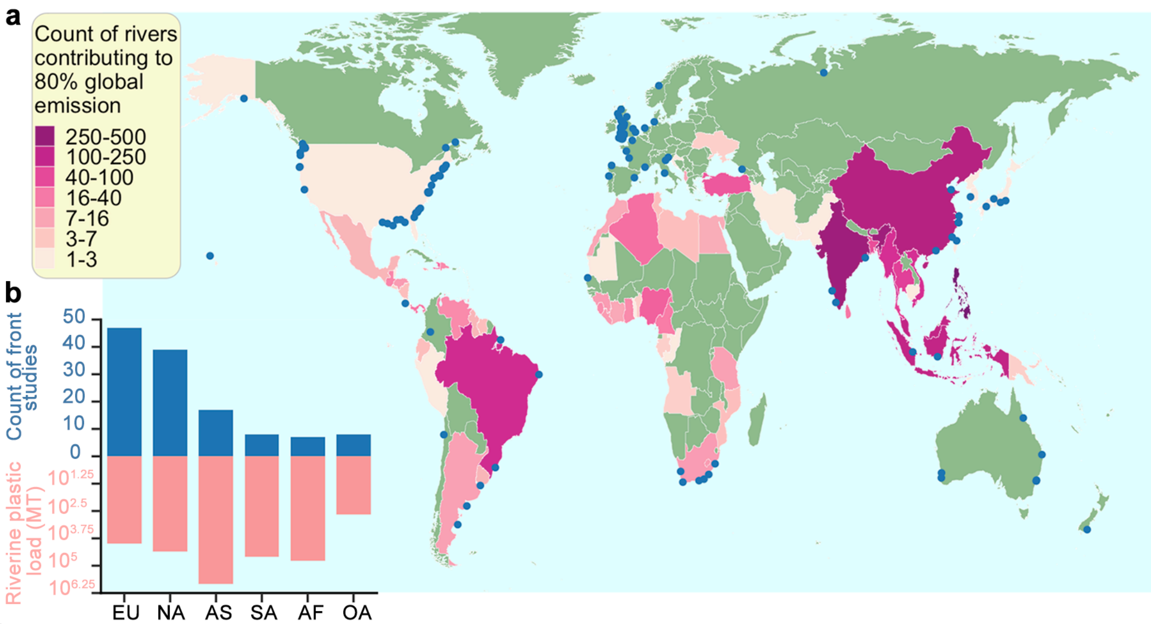

Fig.4 | Global research of estuarine fronts and riverine plastic flux. a | The global map with each country shaded according to the number out of 1656 rivers for 80% of the total plastic flux to the ocean. The annual plastic emission into the ocean emitted by 1656 rivers in total is ~0.8 million metric tons (MT)[7]. Countries not included any of the 1656 rivers are shaded green. Blue dots indicate the locations of estuaries (n=126) where the fronts have been studied in 172 publications (Supplementary Table 2). **b |** The number of estuaries where estuarine fronts are reported (n=126; blue bars) and annual plastic emission into the ocean emitted by 1656 rivers (pink bars) in each continent (Europe, EU; North American, NA; Asia, AS; South America, SA; Africa, AF; Oceania, OA). Currently, research of estuarine fronts is mainly conducted in Europe and North America (blue bars). Annually, the largest contributing continent is Asia with 1278 rivers emitting 60,542 MT, followed by Africa with 60,542 MT through 145 rivers, South America with 39,572 MT through 108 rivers, North America with 22,468 MT through 85 rivers, Europe with 9436 MT through 46 rivers, and Oceania with 445 MT through 2 rivers. The striking mismatch between the geographical location of studies on estuarine fronts and main rivers responsible for plastic loads into the ocean suggests that urgent efforts on understanding processes in estuarine front are required for the mitigation of riverine plastic debris in 'hotspots' like the Asian and African continents.

Box 1 | Encounter kernel rate of particles in aquatic systems

Collision of particles in turbulent flow fields is a physical process bringing particles into contact with each other[84]. The encounter kernel rate of particles determines the rate of collision between particles, which generally depends on three transport processes[81,85], including Brownian diffusion (β_{Br}), fluid shear (β_{sh}) and differential sedimentation (β_{ds}). Brownian diffusion is the random motion that brings particles together through thermal effects. Fluid shear in which velocity gradients occur, induces interparticle contact among the particles carried by the fluid. Collision by differential sedimentation occurs when two particles have different settling velocities due to the gravity effects[204]. The total encounter kernel rate (β_{ij}) between two particles of size i and j is their sum[4]:

$$\beta_{ij} = \beta_{Br}(i,j) + \beta_{sh}(i,j)) + \beta_{ds}(i,j)$$

$$\beta_{Br}(i,j) = \frac{2kT\left(r_i+r_j\right)^2}{3\mu\left(r_i \cdot r_j\right)};\ \beta_{sh}(i,j) = 1.3\sqrt[2]{\varepsilon/\nu}\cdot(r_i+r_j)^3;\ \beta_{ds}(i,j) = \pi(r_i+r_j)^2\left|\omega_i-\omega_j\right|$$

where k is Boltzman constant; T is the absolute temperature; μ and ν are the dynamic and kinematic viscosities, respectively; ε is the turbulent kinetic energy dissipation rate, and ω_i is the settling velocity of a particle with radius r_i.

These encounter kernel rates by three mechanisms vary with particle sizes. The kernel rate by Brownian motion plays a minor role in bringing particles (>1 μm) together[81], thus it is not included to explain the collision rate of microplastics. As particle size increases, collisions arising from shear (either turbulent or laminar) and differential sedimentation, become more important[82]. Shear-induced collision is known to be stronger than other transport mechanisms[83], and was demonstrated to be important in the high particle concentration and high shear environment of the boundary layer[82]. Therefore, strong turbulent energy and high particle load at estuarine fronts can facilitate higher collision rates between plastic and other particles, leading to particle aggregation and/or plastic fragmentation through the surface ablation mode[69,70] (FIG. 3b).