

## REVIEW

## Plastics in the Earth system

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Plastic contamination of the environment is a global problem whose magnitude justifies the consideration of plastics as emergent geomaterials with chemistries not previously seen in Earth's history. At the elemental level, plastics are predominantly carbon. The comparison of plastic stocks and fluxes to those of carbon reveals that the quantities of plastics present in some ecosystems rival the quantity of natural organic carbon and suggests that geochemists should now consider plastics in their analyses. Acknowledging plastics as geomaterials and adopting geochemical insights and methods can expedite our understanding of plastics in the Earth system. Plastics also can be used as global-scale tracers to advance Earth system science.

Humanity, through its development of novel chemical reactions and the sheer magnitude of its activities, is having an ever-growing impact on Earth's elemental cycles. Through this great acceleration (1), we have ushered in a new age in Earth's history: the noosphere or Anthropocene (2, 3). This is an age in which the trajectory of the Earth system is shaped as much by humans as by all other life (4) and in which we are increasingly conscious of our role in modifying the global environment and of our potential to influence

Earth's future. Plastics, a suite of synthetic polymers, are exempla of this new age. Just as fossils indicate when different life-forms emerged, preserved plastics will provide a geological record of humanity's rise to global prominence (4). It has become clear that plastics are an emerging contaminant that may harm organisms and ecosystems not adapted to their presence. Numerous reviews present the potential deleterious effects of plastics (5–9). Here, instead, we discuss plastics as an emergent carbon-based geomaterial—specifically, a new form of anthropogenic detrital, nonliving OC. We discuss plastic distribution, transport, and eventual loss from the Earth system; how contamination of environmental samples by plastics might affect OC studies; how applying concepts and methods from the geosciences might accelerate our understanding of plastics; and how the study of plastics may advance fundamental biogeochemical knowledge.

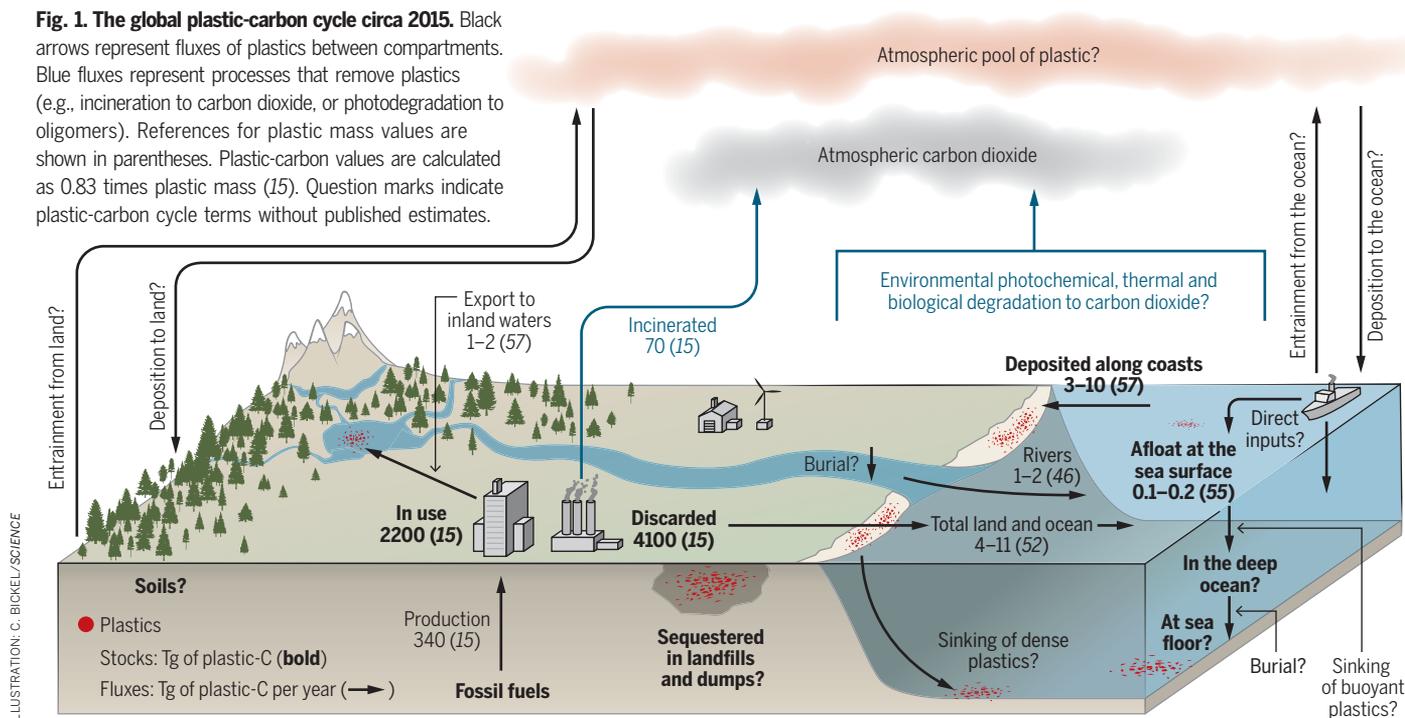
## The plastic-carbon cycle

Biogeochemistry details the cycling of elements at scales ranging from the organismal to the planetary. Arrow diagrams can detail elemental stocks, sources, fates, and transformations (Fig. 1). The cycling of one specific element, carbon, is of particular biogeochemical and societal significance. Organic carbon (OC) fuels life and forms the elemental backbone of biomolecules. Use of OC stored in fossil fuels drives our economy, provides raw materials for the production of most plastics (6), and is warming the planet (10). Thus, in concurrence with a growing literature (11, 12), we present plastics as an emergent component of Earth's carbon cycle.

Different polymers have different carbon contents, depending on their elemental composition (Table 1). Furthermore, additives and processing in the environment may modify plastic carbon content. For instance, oxidation adds oxygen and noncarbon mass to plastics (13, 14). Therefore, precise conversion of plastic mass to plastic-carbon (plastic-C) will require knowledge of the contributions that different polymers make to each global stock and flux, plus empirical measurements of polymer carbon content in the environment. The carbon content of materials is usually determined by elemental analysis, but these analyses are rare for environmental plastics. One study reported homogenized microplastics from North Pacific Gyre surface waters to be 83% carbon by mass (14), a percentage we adopt here to calculate the carbon content of plastic mass. As plastic production and disposal have presumably increased since the data reviewed in this paper were collected, our estimates of

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**Fig. 1. The global plastic-carbon cycle circa 2015.** Black arrows represent fluxes of plastics between compartments. Blue fluxes represent processes that remove plastics (e.g., incineration to carbon dioxide, or photodegradation to oligomers). References for plastic mass values are shown in parentheses. Plastic-carbon values are calculated as 0.83 times plastic mass (15). Question marks indicate plastic-carbon cycle terms without published estimates.



plastic-carbon are likely conservative lower bounds.

From a geochemical perspective, the plastic-carbon cycle (Fig. 1) begins with industrial production of high-molecular-weight polymers and ends when plastics degrade into low-molecular-weight, nonpolymeric compounds, including dissolved and gaseous products (Fig. 2). Large-scale plastics production began around 1950 and has accelerated ever since (Fig. 3). As of 2015, 6.9 Pg of plastic-carbon (Pg-C) had been produced, with 2.2 Pg-C in use, 4.1 Pg-C discarded, and 0.6 Pg-C incinerated (15). The 6.3 Pg-C of plastic that has accumulated (production minus incineration) exceeds human (0.06 Pg-C) and total animal (2 Pg-C) biomass (Fig. 3) (16) but remains modest compared with global OC pools, such as those for soil OC (1500 to 2400 Pg-C) and oceanic dissolved OC (~700 Pg-C) (10). However, plastics have accumulated in mere decades (15), whereas OC has accumulated slowly, often over millennia (10). Examination of annual plastic-carbon fluxes highlights the relevance of plastics to the current carbon cycle.

Most environmental research focuses on the 0.05 to 0.08 Pg-C year<sup>-1</sup> of mismanaged plastics

dispersed to natural systems (17). However, total plastic accumulation includes all in-use and discarded plastics. As of 2015, estimated global plastic production was ~0.34 Pg-C year<sup>-1</sup> with ~0.07 Pg-C of plastics being incinerated (15), the latter of which is equivalent to <1% of anthropogenic CO<sub>2</sub> emissions from fossil fuel burning and cement production (~8 Pg-C year<sup>-1</sup>) (10). The difference between production and incineration indicates that plastics accumulated at 0.26 Pg-C year<sup>-1</sup> in 2015, which is modest compared with global net primary production (~105 Pg-C year<sup>-1</sup>) (18). However, OC accumulations in inland waters (~0.2 Pg-C year<sup>-1</sup>) (10), deep ocean sediments (~0.2 Pg-C year<sup>-1</sup>) (10), forest ecosystems (~0.2 Pg-C year<sup>-1</sup>) (19), and coastal systems (in the form of blue carbon; ~0.1 Pg-C year<sup>-1</sup>) (20) are studied because of their significance in the carbon cycle, yet each of these is slower than current plastic-carbon accumulation. As the accumulation of plastics will likely accelerate into the future (Fig. 3), plastics will become increasingly prominent carbonaceous geomaterials. To understand plastics distributions and impacts, their transport and reactivity must be defined.

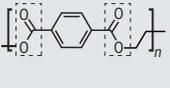
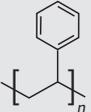
## Transport and degradation

Natural inorganic sediments, such as quartz clays, silts, and sands (density: ~2.65 g cm<sup>-3</sup>), are denser than common plastics (Table 1) (21). Thus, plastics in soils or sediments may remain near the surface, making them vulnerable to mobilization. Surface chemistry (e.g., hydrophobicity), size, and shape further affect location and movement by influencing plastic aggregation with other soil components (21, 22). Bioturbation, ploughing, and water flow can work plastics into soils (21). Deposition in areas with high burial rates can stabilize OC deposits (23) and may do likewise for plastics.

Density, size, shape, and processing influence particle transport (Fig. 4). Whereas most natural sediments are denser than fresh water (~1 g cm<sup>-3</sup>) and seawater (~1.035 g cm<sup>-3</sup>), plastic densities vary by polymer (Table 1). Pure polyethylene (PE) and polypropylene (PP) are buoyant, but solid polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC) are denser than water. Polymer density is modified by additives and drastically reduced by foaming (e.g., as in expanded PS) (24). Shape is defined by how closely a particle resembles a sphere (sphericity) (25) and the smoothness of its edges (roundness) (26). Smaller, less spherical, and more angular particles (e.g., fibers, sheets) have higher surface-area-to-volume ratios and should therefore remain in suspension more readily than larger, more spherical, and more rounded particles (e.g., beads, blocks). In air and, for plastics that sink, in water, particles tend to accumulate at the underlying surface with smaller, less spherical, more angular particles being preferentially mixed into the media as flow increases. Conversely, buoyant plastics should accumulate at the water's surface when waters stagnate with smaller, less spherical, more angular particles being preferentially mixed to depth as turbulence increases (Fig. 4). Aggregation and biofouling also modify the effective density, shape, size, and surface chemistry of plastics, with ramifications for transport (8). Complicating these relationships further, the degree of aggregation and biofouling is modified by particle density (e.g., as it relates to the environment the particle is in), shape, size, and surface chemistry.

Plastics can be degraded via mechanical, photochemical, thermal, and biochemical mechanisms (27). Polymer chemistry is key to determining degradability (Table 1). Additives and the crystal versus amorphous nature of polymers modify their degradability (24). Physical properties include elongation at break, which describes the ability of a plastic to resist cracking, and the glass transition temperature, below which plastics become brittle (24). PS is prone to mechanical fragmentation (28), as it is glassy at environmental temperatures, whereas PE remains nonglassy to ~-100°C and can be elongated nine times its length before breaking (Table 1).

**Table 1. Some material properties of the most abundant plastics on Earth.**

Polymer	Polyethylene (PE)	Polypropylene (PP)	Polyethylene terephthalate (PET)	Polyvinyl chloride (PVC)	Polystyrene (PS)
Elemental formula	(C <sub>2</sub> H <sub>4</sub> ) <sub>n</sub>	(C <sub>3</sub> H <sub>6</sub> ) <sub>n</sub>	(C <sub>10</sub> H <sub>8</sub> O <sub>4</sub> ) <sub>n</sub>	(C <sub>2</sub> H <sub>3</sub> Cl) <sub>n</sub>	(C <sub>8</sub> H <sub>8</sub> ) <sub>n</sub>
Backbone structure					
Bond type	C-C	C-C	Hydrolyzable ethylene	C-C	C-C
Carbon content	86%	86%	63%	38%	92%
% Plastics					
production (2002–2014) (15)	36% by mass 40% by C	21% by mass 23% by C	10% by mass 8% by C	12% by mass 6% by C	8% by mass 9% by C
Density (g cm <sup>-3</sup> ) (24)	0.92–0.97	0.88–0.91	1.30–1.40	1.35–1.50	1.04–1.50 Foamed: <0.05
Photoreactivity (24)	Medium	Medium	Medium	Low	High
Bioreactivity (34)	Low	Very low	Medium	Very low	Low
Glass transition temperature (24)	-110°C	-20°C	75°C	60°–100°C	90°C
Elongation at break (24)	200–900%	150–600%	30–70%	25–80%	1–4%
Limiting oxygen index (24)	17–18%	17–18%	23–25%	40–45%	17–18%
Flammability	Burns indefinitely in air	Burns indefinitely in air	Burns for <30 s in air	Burns for <10 s in air	Burns indefinitely in air

Mechanical fragmentation reduces particle size and increases surface area.

Photochemistry is cited as the most effective chemical degradation pathway for plastics in the environment (13, 27). To photodegrade, materials must contain or interact with chromophores that absorb photochemically active sunlight. Aromatic compounds are the dominant chromophores in natural waters (29). PS contains aromatic chromophores, which may explain its relatively high photodegradability (Table 1). PP and PE are also photoreactive (14, 24), but pure PP and PE contain no chromophoric groups (27); instead, their photoreactivity is attributed to chromophoric impurities, including additives, aromatics absorbed from the environment, and oxidized groups incorporated into polymers during thermal processing (27). Photodegradation of many organics follows first-order kinetics, with rates slowing with increasing exposure (29). By contrast, plastics photodegradation often accelerates, leading to increasingly efficient removal the longer plastics reside in sunlit environments (14). The acceleration in rates may arise from the accumulation of photoreactive oxidized groups as plastics photooxidize, plus an increase in surface area-to-volume ratio as plastics photofragment (13, 14).

Thermal oxidation is slow at ambient temperatures (27). However, many plastics are flammable upon ignition at atmospheric oxygen concentrations (i.e., they have a limiting oxygen index of <21%) (Table 1) (24). Thus, thermal degradation should be rapid during wildfires and biomass burning. Efficient thermal degradation may also occur in geothermal settings, although supply of plastics to these hotspots likely limits realized rates. Both thermal and photodegradation oxidize plastics, reduce polymer molecular weights, produce gaseous products (30–32), and yield soluble organics (30, 33) that can either promote or inhibit microbial growth (13, 14, 33).

Plastics are a potential energy source for heterotrophs. To degrade plastics and access this energy, heterotrophs must break the bonds that bind plastics' polymeric chains. Common hydrolytic enzymes can break ester and urethane bonds in PET and polyurethane (34). However, plastics with carbon-to-carbon (C–C) bonded chains are more bioresistant (Table 1). Intestinal microbes of some insect larvae, plus some rare, free-living microbes, can degrade C–C bonded PE and PS under laboratory conditions, but it remains unclear whether these rates are ever realized in nature (34). The enzymes that degrade C–C bonded plastics remain enigmatic. Enzymes capable of C–C bond cleavage evolved to degrade lignin, a polymeric component of wood, and can slowly degrade PE (34). It appears to have taken 125 million years for lignin-degrading enzymes to evolve after lignin emerged in the fossil record (35). By contrast, some bacteria have already adapted existing lipases and cutinases to utilize PET

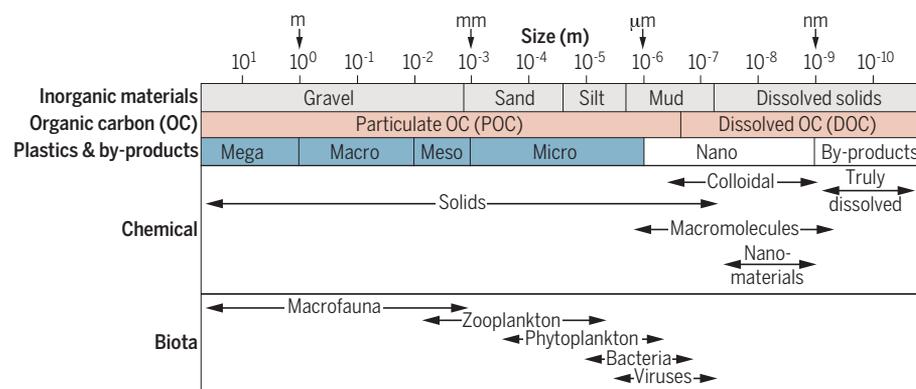
(36, 37). However, these PETase genes remain rare in microbial communities (36) and target PET's ester bonds. Thus, it is unclear whether PET degradation will become widespread or whether similar evolutionary shortcuts can be found for the biodegradation of other plastics, particularly those with stronger C–C bonds. Furthermore, despite emerging ~400 million years ago (35), lignin is still sufficiently resistant to enable trees and houses to stand for centuries and to allow for its accumulation in soils and sediments (38). Thus, lignin and plastics will likely resist efficient biodegradation for some time to come.

The transport and degradation pathways of plastics are intimately linked. Photo-, thermo-, and biodegradation oxidize plastics, increasing subsequent photodegradability and biodegradability, and promote fragmentation, altering plastic size distributions with ramifications for transport, distribution, and reactivity. Transport moves plastics between Earth's three physical compartments—land, atmosphere, and

water. In each compartment, plastics may have different biogeochemical impacts and be exposed to different environmental conditions, the latter of which impacts plastic degradation and fate. The amount and size distributions of plastics also influence OC studies. For instance, if plastics are analyzed as an unacknowledged fraction of OC, OC concentrations and storage may be overestimated (12, 39). Furthermore, geochemists use radiocarbon to date OC, and plastics are overwhelmingly produced from ancient, radiocarbon-dead fossil fuels. Thus, when occurring in OC samples, plastics will increase the sample's apparent age, influencing perceived OC accumulation and turnover rates.

### Plastics on land

Most discarded plastic-C is added to landfills and open dumps (6). Just as natural OC in soils, ocean sediments, or fossil fuel stores can remain sequestered until disturbed, plastics should remain sequestered in well-designed



**Fig. 2. Size ranges for geomaterials, including plastics.** Inorganic materials include gravel, sand, silt, mud, and dissolved solids. Organic carbon is commonly operationally defined as either particulate or dissolved. Plastics are divided into mega-, macro-, meso-, micro-, and nanoplastics, plus the nonplastic by-products of plastic degradation. Commonly applied size distributions for chemical classes and for biota are also included.

**Table 2. Potential plastic-carbon contributions to detrital, nonliving organic carbon (OC) concentrations.**

Environment	OC	Plastic-C	Units	% Plastic-C*
<i>Surface soil OC</i>				
Floodplain	8.2 (42)	0.004–0.046 (41)	g-C kg <sup>-1</sup>	0.1–0.6
Industrial	8.2 (42)	0.25–56 (43)	g-C kg <sup>-1</sup>	3–87
<i>River particulate OC</i>				
Global export	100–400 (10)	1–2 (47)	Tg-C year <sup>-1</sup>	0.2–2.0
Amazon, Brazil	5 (48)	0.03–0.05 (47)	Tg-C year <sup>-1</sup>	0.5–1.0
Brantas, Indonesia	0.015 (49)	0.03–0.05 (47)	Tg-C year <sup>-1</sup>	64–78
<i>Ocean subtropical gyre surface water particulate OC</i>				
North Pacific Ocean	26 (50)	0.03–34 (51)	μg-C liter <sup>-1</sup>	0.1–57

\*Assumes OC and plastics are independently quantified fractions of total nonliving OC [i.e., calculated % plastic-C = plastic-C ÷ (OC + plastic-C)].

landfills. However, landfills and dumps are important to study as hotspots of plastic-C accumulation on Earth; as regions of potential plastics erosion and export; to understand the ecological and geomorphologic implications of plastics being a major geomaterial in an ecosystem; and as crucibles forging plastic-degrading life-forms. Plastics enter other soils as mismanaged waste and in sewage-derived fertilizer (40). Plastic mass in soils remains poorly constrained and has not been compared with total soil OC within any single sample. In lieu of these data, we compare the scant data on plastic mass in soil to OC measured in similar soils. In Swiss floodplain soils, this gives an estimated plastics contribution of 0.1 to 0.6% (41, 42), whereas plastics may dominate OC stocks in industrially contaminated soils (43) (Table 2). Addition of plastic-carbon to soils may lead to overestimates of OC accumulation and radiocarbon ages. Plastics in soils can alter soil aggregation and larger items may alter flow paths, influencing the formation, stability, and hydrology of soils (22). The decrease in soil density when adding plastics can promote plant growth, whereas leaching of additives may harm plants (22). Thus, changes to carbon loading, soil structure, hydrology, and chemistry in soils amended with plastics will likely alter biogeochemical cycles, including primary production and nutrient cycling (22). Whether these effects are significant outside of heavily impacted systems is unclear.

### Plastics in the atmosphere

Micro- and nanoplastics (Fig. 2) are found throughout the atmosphere, including in the air we breathe (44). Atmospheric studies of ~50- to 5000- $\mu\text{m}$  particles indicate that plastics at the smaller end of this range are most

numerous. Deposition is high near urban and industrial sources (44), but the low density of plastics compared with natural dust facilitates their long-range transport (45). Spatial patterns in the sizes, shapes, and chemistries of deposited plastics and how they covary with atmospheric conditions offer insight into the distribution and sources of plastics in the atmosphere. However, current knowledge is insufficient to allow plastics to be incorporated into atmospheric transport and chemistry models. Such studies are required to understand the atmospheric fate of plastics and how plastics affect air quality and planetary albedo.

### Plastics in inland waters

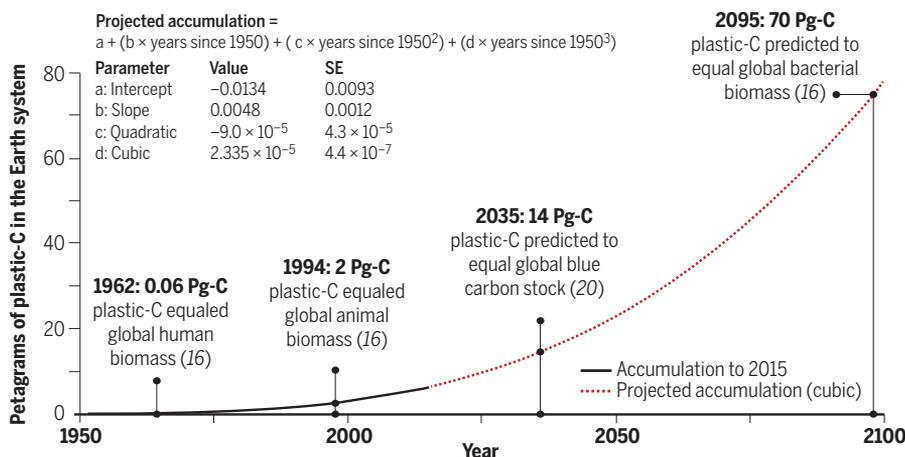
Plastics can enter inland waters as mismanaged waste from land, as direct inputs (e.g., discarded fishing equipment), and through the erosion of soils, landfills, and in-use plastics (e.g., buildings) (6). Once entrained, plastics can settle out and accumulate in sediments when water slows (e.g., in reservoirs) (46), be degraded in the water column, or be exported to sea (47). Empirical data for the mass of plastics exported by rivers remain limited. However, a risk analysis estimated that 1.0 to 2.0 Tg plastic-carbon is carried through rivers to the sea annually (47) (Fig. 1). This equates to 0.2 to 2.0% of global riverine fluxes of particulate organic carbon (POC) (10) but varies for individual rivers (Table 2). For instance, although the Amazon River is estimated to carry the seventh-largest load of riverborne plastics (47), plastics equate to <1% of POC in this massive river (48). By contrast, small, urbanized rivers (e.g., the Brantas) may export more plastics than biogenic POC (Table 2) (47, 49). The Brantas drains a catchment >500 times smaller than the Amazon yet exports a greater mass of plastics (47). Thus, the contri-

bution of small, urbanized rivers to global plastic export appears oversized compared with their drainage areas. Addition of plastic-C may also alter the fluxes, chemistry, and apparent ages of OC in rivers.

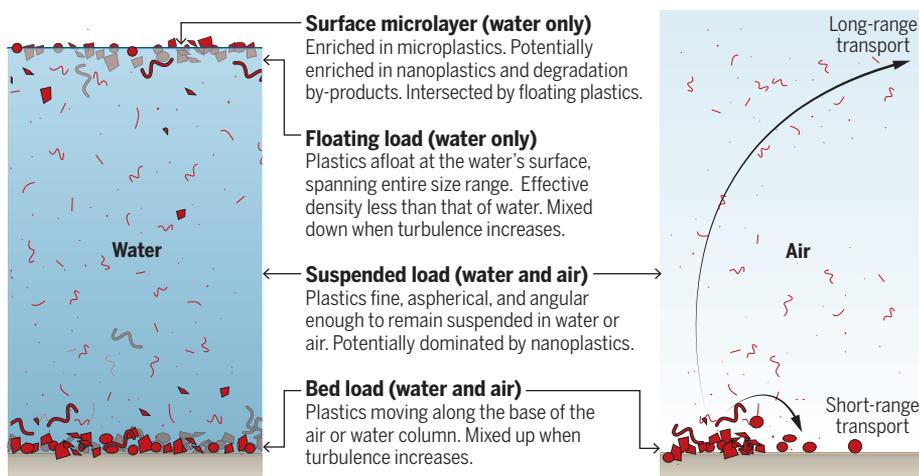
### Plastics in the ocean

Sources, stocks, and sinks of plastics are not yet reconciled at sea. Sources include rivers, other coastal inputs, atmospheric deposition, and direct inputs (e.g., jetsam, flotsam, and derelict). A risk analysis suggests that 4.0 to 10.5 Tg of plastic-carbon entered the oceans in 2010 (50) (Fig. 1). About 40% of plastics entering the ocean are expected to sink on the basis of polymer type (51). Hotspots of sinking plastic accumulation have been identified in coastal and deep ocean sediments (52, 53). However, global estimates of plastics in marine sediments do not exist. The other 60% of plastics entering the oceans should float initially. Floating plastics are usually sampled in the upper 0–10 cm to 0–100 cm of the ocean using tow nets that capture particles larger than ~300  $\mu\text{m}$  (8). Estimated standing stocks of surface plastics total 0.07 to 0.20 Tg-C (54). According to estimates of inputs and stocks, <10% of buoyant plastics entering the oceans each year are found afloat at sea. This accounting gap may result from overestimated inputs; underestimates of floating plastics (net tows only sample the upper meter of the ocean and mainly collect microplastics); and the loss of floating plastics from surface waters via photodegradation, shoreline deposition, consumption by marine life, and sinking due to aggregation with POC, egestion in fecal pellets, or biofouling (8).

In contrast to surface plastic sampling, oceanic POC is usually sampled at depths >1 m by pre-filtering to remove zooplankton (>202  $\mu\text{m}$  in size) and then filtering through sub-micrometer filters to collect POC (Fig. 2) (55). Acknowledging these differing approaches, we compare plastic and POC concentrations in subtropical gyre surface waters where ocean physics drive the accumulation of plastics (8). In the North Pacific Subtropical Gyre, areal surface concentrations of 500- to 5000- $\mu\text{m}$  microplastics sampled from the upper 15 cm of the water column ranged from 0.03 to 34  $\text{kg km}^{-2}$  (51), which equates to a per-volume carbon concentration of 0.1 to 21.9  $\mu\text{g-C liter}^{-1}$  (average: 4.7  $\mu\text{g-C liter}^{-1}$ ). POC concentrations in the upper 5 m of the North Pacific at Station ALOHA average  $26 \pm 7 \mu\text{g-C liter}^{-1}$  (50). Assuming microplastics and POC were sampled as distinct fractions, microplastic-carbon may make up 0.1 to 57% (average: 15%) of the total particulate nonliving OC in surface waters of the North Pacific Subtropical Gyre (Table 2). The variation in this range illustrates the patchiness of marine debris, while the upper estimate and average highlight the potential significance of plastic-carbon at the ocean's surface. An abundance of plastics at the sea



**Fig. 3. Accumulation of plastic-carbon in the Earth system.** Accumulation of plastic up to 2015 calculated as production minus incineration (15). Projected accumulation calculated assuming current trend (cubic growth) for plastic accumulation will continue into the future. The cubic model had the lowest Akaike information criterion of models in JMP. Actual future plastic-carbon accumulation will depend on hard-to-predict socioeconomic factors. Biomass numbers refer to living biomass.



**Fig. 4. Distribution of plastics in water and air.** In water, four layers are considered: the surface microlayer, the floating load (the most often studied fraction in water), the suspended load (seldom studied in water), and the bed load (somewhat studied in water as deposited materials). Plastics that are less dense than water tend to float and become concentrated in the surface microlayer and floating load, whereas plastics that are denser than water tend to accumulate in the bed load. All plastics are denser than air. Thus, in air, only two layers are considered: the suspended load and the bed load.

surface may affect the ecology and biogeochemical function of a layer that covers two-thirds of the planet's surface, with potential impacts on atmospheric chemistry in the marine boundary layer, surface ocean ecology, and ocean biogeochemistry (56).

### Accelerated learning

Our estimate of plastic accumulation on Earth assumes that industrial incineration is the only sink (Fig. 3). Environmental degradation also converts plastic-carbon to non-plastic-carbon (e.g., gases and nonpolymeric organics). However, robust estimates of net plastic removal via environmental processes remain unattainable while fundamental information about plastic distribution and reactivity is lacking. Developing this quantitative, mechanistic understanding of the global plastic cycle will require data for the occurrence, flux, and transformation of different polymers in each compartment of the Earth system. To facilitate this, collection and analysis of plastics should be standardized across systems, and studies should report plastic mass along with polymer type and particle size. Improved data for the distribution of plastics must be augmented with quantitative studies of degradation in each environment.

Empirical data on plastic-mass distributions are scarce. Models predict fluxes and distributions for some terms in the global plastic cycle (Fig. 1). Existing knowledge concerning geomaterials can be leveraged to predict gradients of plastics in other systems. By modeling or consulting the geoscience literature first, onerous fieldwork can be designed to test model predictions or focus on hypothesized hotspots of plastic cycling and impact. In this Review, we highlight landfills and dumps, areas of atmo-

spheric and aquatic deposition, urban rivers, and the sea surface as potential sites of major importance for plastic accumulation, transport, degradation, and biogeochemical impact.

In the 1950s, nuclear weapons testing enriched the atmosphere with radiocarbon. This bomb spike obfuscated natural radiocarbon signals, complicating the dating of OC after 1950. However, the bomb spike also represented a new, temporally explicit tracer that helped resolve aspects of ocean circulation and OC cycling. Today, adding explicit analysis of plastics to OC studies would ensure that OC concentrations, ages, and chemistries are correctly interpreted, particularly in plastic-rich systems. However, the temporally resolved emergence of plastics as geomaterials with distinctive physical and chemical characteristics can also be leveraged as a tracer experiment to test our knowledge of particle and carbon cycling in the Earth system. Thus, while the study of the global plastic cycle is critical to understanding the environmental impact of plastics, it also offers an opportunity for geochemical insight to be gained.

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