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The Ocean's labile DOC supply chain

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Abstract

Microbes of the surface ocean release, consume, and exchange labile metabolites at time scales of minutes to days. The details of this important step in the global carbon cycle remain poorly resolved, largely due to the methodological challenges of studying a diverse pool of metabolites that are produced and consumed nearly simultaneously. In this perspective, a new compilation of published data builds on previous studies to obtain an updated estimate of the fraction of marine net primary production that passes through the labile dissolved organic carbon (DOC) pool. In agreement with previous studies, our data mining and modeling approaches hypothesize that about half of ocean net primary production is processed through the labile DOC pool. The fractional contributions from three major sources are estimated at 0.4 for living phytoplankton, 0.4 for dead and dying phytoplankton, and 0.2 for heterotrophic microbes and mesoplankton.

Oceans are the source of ~ 63 Pg (10^{15} g) of newly fixed carbon each year, accounting for about half of global net primary production (NPP) (Behrenfeld et al. 2005). This estimate is derived from satellite remote sensing data, which provide broad spatial and temporal coverage of the global oceans and is site-validated with in situ measurements. However, what happens next in the ocean carbon cycle is not as well constrained, particularly regarding the entrainment of recently fixed carbon into the dissolved organic carbon (DOC) pool. This poorly resolved area of ocean biogeochemistry can be traced to the many complex roles of the "microbial loop" (Azam et al. 1983) in which DOC is rapidly released, consumed, repackaged, and mineralized by the surface ocean microbiome. Our understanding of the microbial loop has in fact been characterized as "inferential," being derived largely from indirect measures of events we cannot observe (Pomeroy et al. 2007).

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What we do know is that recent photosynthate enters the ocean's food webs as either particulate organic carbon in the form of phytoplankton cell biomass (particulate primary production [PPP]) or as DOC released from phytoplankton through the course of growth and maintenance (dissolved primary production [DPP]) (Box 1). Together, the PPP and DPP pools make up the total primary production (TPP) of the ocean system. We also know that processing of DPP carbon is largely the domain of heterotrophic bacteria, the organisms best able to access highly dilute low-molecular-weight compounds in seawater (although see Palenik and Morel 1990; Zubkov et al. 2003; Orellana et al. 2019; Tully 2019; Baltar et al. 2021). Yet, phytoplankton DPP is not the only source of labile DOC to bacteria, since activities of various heterotrophic microbes, mesofauna, viruses, and fungi in the microbial loop also release metabolites into seawater, supplementing the more direct supply of labile molecules from living phytoplankton. Once consumed, DOC is inefficiently assimilated by bacteria and the majority of carbon is oxidized back to CO_2 via respiration (del Giorgio et al. 2011) for eventual equilibration with the atmosphere. Thus, from the viewpoint of ocean carbon sequestration, bacterial processing of recently fixed organic matter through the labile DOC pool is the main mechanism by which carbon is excluded from long-term storage in the ocean.

The ocean's DOC reservoir is large (~ 622 Pg C; Hansell 2013) and chemically diverse (tens of thousands of unique compounds; Hertkorn et al. 2013). Ordered from least to most biologically labile, the molecules in marine DOC are

Box 1. Glossary.

DOC – dissolved organic carbon.
TPP – total primary production. Organic carbon accumulated by photosynthetic or chemosynthetic autotrophs (= NPP)
NPP – net primary production. Organic carbon accumulated by photosynthetic or chemosynthetic autotrophs (= TPP)
PPP – particulate primary production. Organic carbon accumulated in particulate (cellular) form by photosynthetic or chemosynthetic autotrophs
DPP – dissolved primary production. Organic carbon released in dissolved form by photosynthetic or chemosynthetic autotrophs
%ER – percent extracellular release. DPP as a percentage of TPP
BP – bacterial production. Synthesis of bacterial biomass from organic precursors
BR – bacterial respiration. Mineralization of bacterial organic matter into inorganic carbon
BCD – bacterial carbon demand. Sum of bacterial production and respiration
BGE – bacterial growth efficiency. The proportion of incorporated carbon converted into biomass, calculated as BP/BCD
Microzooplankton – planktonic protists and animals < 0.2 mm in size
Mesozooplankton – planktonic animals in the size range 0.2–20 mm
ESD – equivalent spherical diameter. Body volume expressed as the diameter of a sphere with equal volume

classified as ultra-refractory, refractory, semi-refractory, semi-labile, and labile (Hansell 2013). The first four categories account for > 99.9% of the DOC pool but only 16% of carbon turnover. The fifth category, labile marine DOC, accounts for < 0.1% of the DOC pool yet 84% of annual DOC turnover (Fig. 1). This pool is defined as the organic molecules with high turnover rates in seawater due to rapid uptake by heterotrophic bacteria (Hansell 2013) and is the focus of this perspective.

Movement of carbon in and out of the labile DOC pool is nearly undetectable given current methodology. Organic carbon is initially released by phytoplankton and other marine microbes in the form of labile metabolites, most likely following a diel pattern that tracks with irradiance (Carlson and Hansell 2015). Within the time span of ~ 3 d (the residence time of a 0.2 Pg C pool size with a 20 Pg C yr^{-1} production rate; Hansell 2013), labile DOC has been transformed by bacteria, with the primary fate being conversion of carbon back into inorganic form (Ducklow et al. 1986). From the perspective of global carbon models, therefore, labile DOC cycling represents a flux that largely cancels itself out, being important only for small leaks that become sequestered in the deep ocean (Raven and Falkowski 1999; Jiao et al. 2010). Yet, because it is also the largest carbon flux in the ocean, a small percent change in the rate of transformation or fate of labile DOC will amount to a nontrivial change in the ocean inventory over decadal time scales (Fig. 1). The same percent change in the rate of carbon accumulation in the deep ocean (currently 2 Pg C yr^{-1} as both DOC and POC; Caldeira et al. 2005) would represent an order of magnitude smaller effect. This argues for increased consideration of the current and future microbial processing of labile DOC.

In this perspective, we generate hypotheses about the amount and comparative importance of sources of labile compounds in the surface ocean. The major recognized sources are metabolites released from (1) living phytoplankton, (2) dead and dying phytoplankton, and (3) heterotrophic microbes and mesoplankton. Three synthesis studies that date back several decades served as the foundation of our analyses: Cole et al. (1988) addressed statistical links between rates of bacterial production (BP) and PPP, Baines and Pace (1991) modeled the relationship between DPP and PPP, and del Giorgio and Cole (1998) compared rates of BP and bacterial respiration (BR), which together define the bacterial growth efficiency (BGE). Our objective was to determine whether the existing literature provides a sufficient basis for a quantitative understanding of the DOC supply chain in the ocean's microbial food web.

A frequent point of ambiguity in ocean carbon budgeting, and one that plagued our literature searches, is the distinction between NPP and PPP. Because many in situ measures of primary production are based on ^{14}C assimilation, which typically does not capture photosynthate released in dissolved form, they best approximate PPP (Baines and Pace 1991; Anderson and Ducklow 2001; Fouilland and Mostajir 2010) rather than NPP. Thus, organic matter released as DPP, while conceptually a component of NPP is often not included in NPP measures. Previous studies on bacterial processing of primary production in aquatic ecosystems have therefore used the term TPP (Baines and Pace 1991; Fouilland and Mostajir 2010), which is defined as the sum of particulate and dissolved primary production, to emphasize distinct accounting of each carbon pool. Here, we follow this lead and use the term TPP rather than the equivalent term NPP to accentuate separate tracking of particulate and dissolved components of primary production (Box 1):

$$\mathrm{TPP(or\,NPP)} = \mathrm{PPP} + \mathrm{DPP}$$

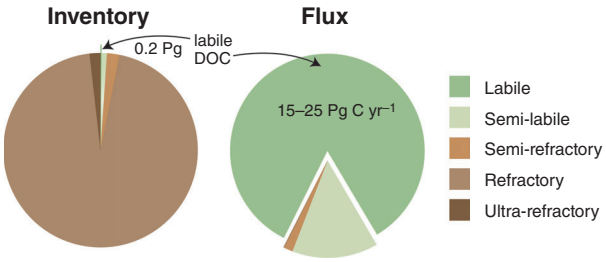


Fig. 1. Ocean inventory (left) and annual flux (right) of five classes of marine DOC. Values apply to the labile fraction, accounting for < 0.1% of the DOC inventory yet 84% of the carbon flux through the DOC pool. Data from Hansell (2013).

For this analysis, we set TPP to 63 Pg C yr^{-1} (Behrenfeld et al. 2005).

Estimates of labile DOC flux from the three major sources were obtained by compiling literature values that calculated, or provided the information for us to calculate, DOC supply as a fraction of TPP, and a steady state model was used to integrate the inputs (the "supply" method). We also separately addressed the utilization side, compiling values of carbon requirements needed to sustain observed bacterial growth in the surface ocean as a fraction of TPP (the "demand" method). Finally, we reconciled these two complementary approaches to hypothesize the relative importance of labile DOC sources in sustaining bacterioplankton communities of the surface ocean. We note at the outset that both significant methodological differences and true ecological variability generated substantial uncertainties around mean values of DOC flux and fate.

The sources

Here, we describe the literature values used to parameterize a "sources" model that sums inputs from the various components of the microbial food web. Where data were sufficient, the model randomly selected one reported value in each iteration. Where data were sparse, parameters were based on an assumed distribution that was randomly sampled, or in a few cases on just a single measure. Many literature values for inputs are reported on the basis of PPP rather than TPP, and in the model structure, PPP varies because it is dependent on the selected value of DPP (i.e., the direct labile DOC release from living phytoplankton is subtracted first). For literature values reported on a PPP basis, conversion occurs within the model to a TPP basis after the DPP parameter has been assigned for that iteration.

Input 1: Labile DOC from living phytoplankton

Although previously debated (Sharp 1977; Smith Jr et al. 1977; Bjørnsen 1988), it is now largely accepted that healthy phytoplankton cells indeed release labile molecules into seawater, and that this release can be biogeochemically relevant (Thornton 2014). Mechanisms of DPP release include both passive processes, such as diffusion across cell membranes (Bjørnsen 1988), and active processes (Fogg 1966; Williams 1990), such as physiological balance during photosynthesis (Wood and Van Valen 1990) or redox homeostasis (Durham et al. 2019). The percent extracellular release parameter (%ER) represents DPP as a percent of TPP:

$$\%\mathrm{ER} = \frac{\mathrm{DPP}}{\mathrm{DPP} + \mathrm{PPP}} \times 100$$

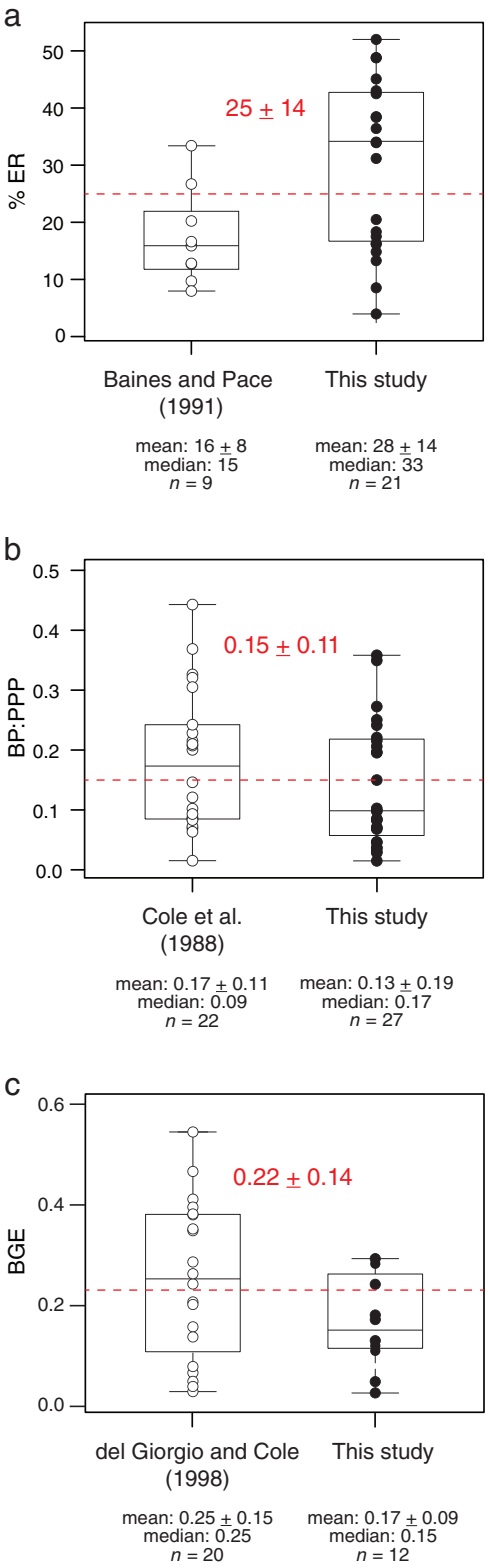
Measures of %ER vary greatly in the literature, with inconsistencies attributed to effects of phytoplankton taxonomy, stress, environmental conditions, and artifacts of sampling protocols (Hellebust 1965; Sharp 1977; Lancelot 1979; Goldman and Dennett 1985; Nagata 2000; Thornton 2014). A trend that emerged from these data is that of a higher fraction of extracellular release in nonproductive ecosystems such as the oligotrophic ocean, reaching 35% or more of TPP, compared to lower and relatively constant release in highly productive systems such as upwelling regions, ranging from 2% to 10% (Baines and Pace 1991; Teira et al. 2001a,b). Despite the substantial variability, a systematic survey of the published values undertaken by Baines and Pace (1991) found an average %ER across studies of 16% of TPP. We asked whether recent literature agrees with this value, examining field studies published after the Baines and Pace (1991) review. From 21 post-1991 studies generating 328 %ER values on a volumetric basis, DPP accounted for an average of 28% of TPP (Fig. 2a; Supplementary Table S1). There was insufficient metadata to distinguish between low- and high-productivity systems in the more recent data. Combining data from pre-1991 (Baines and Pace 1991) and post-1991 (this study), the mean value of DPP release is 25% of TPP with a range of 3–50%.

Input 2: Labile DOC from dead and dying phytoplankton

Viral infection is an important top-down control over microbial growth in the surface ocean (Fuhrman 1999; Zimmerman et al. 2020), yet quantitative estimates of labile DOC contributed by this process are scarce. The current conceptualization of carbon fate following viral activity is termed the "viral shunt," in which cell carbon is converted to both nonliving POC in the form of recalcitrant cellular components such as cell walls, and labile DOC in the form of nucleotides, amino acids, sugars, and lipids (Suttle 2007). Viral reprogramming of phytoplankton host cells can alter lipid composition (Rosenwasser et al. 2014), nucleic acid synthesis rates (Rosenwasser et al. 2014; Thamatrakoln et al. 2019), and extracellular polysaccharide production (Nissimov et al. 2018), as well as the pool of DOC released post-lysis (Ma et al. 2018; Zhao et al. 2019; Kuhlisch et al. 2021). A model by Jumars et al. (1989) simulating labile DOC release from phytoplankton was revised by Wilhelm and Suttle (1999) to include viral lysis. The revised model predicts that 2–10% of TPP is passed

through the viral shunt (Suttle 1994, 2007; Fuhrman 1999; Wilhelm and Suttle 1999). Another modeling study used parameters estimated from laboratory dilution experiments to predict that one third of phytoplankton carbon passes through the viral shunt (Talmy et al. 2019), three times higher than the Wilhelm and Suttle model but with large uncertainty among modeling solutions. Experimental laboratory studies characterizing dissolved organic matter release with cultivated virus–host pairs are still few in number (Zimmerman et al. 2020). Using the range of predictions from Wilhelm and Suttle (1999), we parameterized phytoplankton viral lysis as a uniform distribution between 2% and 10% of TPP (Fig. 3; Table 1).

Grazing by zooplankton of intact phytoplankton cells (PPP) releases labile DOC from physical breakage, a process referred to as "sloppy feeding" (Strom et al. 1997; Møller 2005, 2007). The smaller size class of zooplankton, or "microzooplankton" (made up primarily of protists < 0.2 mm, with ciliates and flagellates as typical model organisms) engulf their prey whole and do not contribute substantially to sloppy feeding. However, the larger size class of zooplankton, or "mesozooplankton" (made up primarily of metazoans 0.2–20 mm, with copepods as typical model organisms) release labile DOC from their phytoplankton prey as a function of size difference, with more DOC generated as predator and prey sizes converge (Møller 2005). Copepods having equivalent spherical diameters (ESDs) 8–33 times larger than their prey (as an example, the average copepod:dinoflagellate ESD ratio is ~ 26:1; Hansen et al. 1997) were shown to have an inverse relationship between ESD and DOC released, with sloppy feeding generating DOC equivalent to 30% of ingested POC for a copepod:prey ESD ratio of 8:1, vs. ~ 5% of ingested POC for a copepod:prey ESD ratio of 33:1 (Møller 2007). Copepods grazing on diatoms with a copepod:diatom ESD ratio of 32:1 released 3% of prey carbon as DOC via sloppy feeding (Saba et al. 2011). Evidence that components of the organic molecules released by sloppy feeding are indeed labile is based on demonstrated stimulation of bacterial growth (Peduzzi and Herndl 1992; Hygum et al. 1997). In our model, sloppy feeding was parameterized as a uniform distribution between 0% and 30% of the carbon in grazed phytoplankton (Table 1), which is inclusive of cases when the predator:prey ratio is



(Figure legend continues on next column.)

Fig. 2. Values for labile DOC parameters in marine ecosystems collected in previous literature surveys (left box plot in each panel, only marine data are included; Cole et al. 1988; Baines and Pace 1991; del Giorgio and Cole 1998) and in this study (right box plot) for (**a**) % extracellular release, (**b**) ratio of bacterial production to PPP, and (**c**) bacterial growth efficiency. The horizontal line indicates the median, the box delineates the two middle quartiles, and the whiskers represent the range. The red dashed line and red font indicates the overall mean for combined data from previous surveys and this study. Panel (**a**), right box plot and the resulting data analysis do not include an outlier of 90% (Hamdan and Jonas 2007); panel (**b**), right box plot and the resulting data analysis do not include an outlier of 0.96 (Lamy et al. 2006).

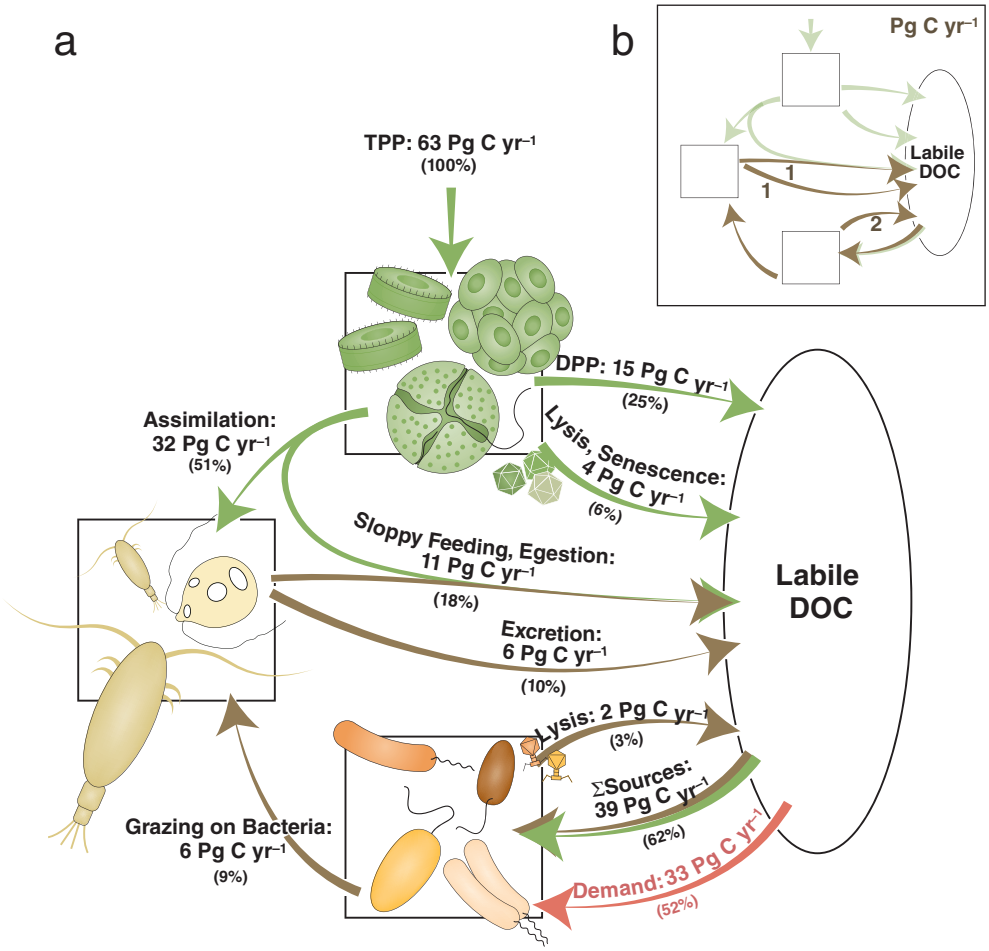


Fig. 3. Two estimates of labile DOC flux into surface ocean heterotrophic bacterioplankton based on TPP equal to 63 Pg C yr^{-1} (Behrenfeld et al. 2005). (**a**) One estimate (ΣSources) is derived from literature values of carbon inputs assigned to various steps in the microbial food web in the form of primary (green arrows) or secondary (brown arrows) production. Values are the mean of 100,000 model iterations. A second estimate (demand) is calculated from the BCD based on mean literature values of heterotrophic bacterial production and growth efficiency in surface marine waters (red arrow). (**b**) Separate accounting of labile DOC inputs derived from recycling in the ΣSources model; these are included in part a. Units are Pg C yr^{-1}.

such that phytoplankton cells are completely ingested (e.g., a copepod:flagellate ESD ratio of 138:1; Hansen et al. 1994).

Egestion is the release of undigested prey carbon that has passed through a gut or food vacuole. The proportion of ingested phytoplankton biomass released as egestion from zooplankton has been estimated at 30% (i.e., 70% of ingested food is assimilated by the organism), although this value varies by taxon and prey nutritional quality, particularly nitrogen content (Steinberg and Landry 2017). Phytoplankton cell material egested by mesozooplankton is packaged as membrane-bound fecal pellets, with labile DOC liberation occurring through coprophagy, microbial enzymatic digestion, and passive leakage (Urban-Rich 1999; Thor et al. 2003). Experiments suggest that > 50% of mesozooplankton fecal pellet carbon is liberated as labile DOC (Urban-Rich 1999). In the case of microzooplankton, prey is hydrolyzed in acidic food vacuoles, and unassimilated organic matter is eventually evacuated along with predator digestive enzymes (Lancelot 1979; Nagata 2000; Steinberg and Landry 2017). Flagellate microzooplankton egestion is in the form of picopellets from which ~ 21% of egesta is estimated to be liberated as DOC (Pelegri et al. 1999). Our model assumed an assimilation efficiency of 70% of phytoplankton carbon, and that the unassimilated egesta lost half its carbon content as labile DOC (Fig. 3; Table 1). Although both sloppy feeding and egestion release rely on the activities of zooplankton for their generation, the resulting DOC is in the form of primary production, that is, phytoplankton organic carbon prior to trophic transfer.

Dead and dying phytoplankton also contribute to the labile DOC pool when lysed during parasitic infections. Unicellular parasites in the Syndiniales are abundant in microeukaryote communities throughout the ocean (Guillou et al. 2008; Lima-Mendez et al. 2015; Clarke et al. 2019). Acting similarly to

Table 1. Parameter values for calculation of labile DOC flux in the surface ocean, including data from review papers by Baines and Pace (1991), Cole et al. (1988), and del Giorgio and Cole (1998), and values published since the date of these reviews (Supplementary Tables S1–S3). Primary parameters are calculated outside the model from published data compiled only from coastal and open ocean ecosystems, using WebPlotDigitizer (Rohatgi 2020, https://automeris.io/WebPlotDigitizer, accessed 02/27/2022) to extract values presented only in figures. See Supplementary Tables S1–S3 for additional information. Derived parameters are determined inside the model from results of 100,000 runs. Calculation equations are populated with parameter letters from the first column. †, one outlier value removed; Micro-Z, microzooplankton; Meso-Z, mesozooplankton; GGE, gross growth efficiency; g_0, ΣSources from the first circuit of the model, *see* the Supply-based estimate section. See Box 1 for other abbreviations.

Primary parameters		Basis	Mean	SD	Median	Min	Max	*n*	Model input	Reference
A	TPP	%TPP	100						Single value	
B	DPP	%TPP	24.5†	13.7	19.1†	2.8	50.0	30	Resampled value	Baines and Pace (1991), this study
C	BP	%PPP	15.1†	11.0	9.8†	0.5	43.9	49	Resampled value	Cole et al. (1988), this study
D	BGE	%BP	21.8	13.5	20.0	3.0	53.7	32	Resampled value	del Giorgio and Cole (1998), this study
E	Phyto lysis by viruses	%TPP				2	10		Random draw from uniform distribution	Wilhelm and Suttle (1999)
F	Micro-Z grazing on phytoplankton	%PPP	62.4	8.6	67.0	49.0	77	11	Resampled value	Schmoker et al. (2013)
G	Sloppy feeding	%Grazed				0	30		Random draw from uniform distribution	Møller (2007)
H	Zoop DOC egestion	%Egested	50						Single value	Urban-Rich (1999)
I	Zoop assimilation efficiency	%Ingested	70						Single value	Steinberg and Landry (2017)
J	Micro-Z GGE – flagellate	%Ingested	32	17		10	63		Random draw from normal distribution	Straile (1997)
K	Micro-Z GGE – dinoflagellate	%Ingested	30	21		4	67		Random draw from normal distribution	Straile (1997)
L	Micro-Z GGE – ciliate	%Ingested	26	12		9	48		Random draw from normal distribution	Straile (1997)
M	Micro-Z transfer efficiency into Meso-Z	%Micro-Z biomass				30	100		Random draw from uniform distribution	Steinberg and Landry (2017)
N	Meso-Z GGE	%Ingested	26	21		1	68		Random draw from normal distribution	Straile 1997
O	Zoop excretion	%Ingested	12						Single value	Saba et al. (2011)
P	Bacterial lysis by viruses	%BP				20	30		Random draw from uniform distribution	Fuhrman (1999); Wilhelm and Suttle (1999)

Derived parameters		Basis	Mean	SD	Median	Min	Max	Calculation
Q	PPP	%TPP	75.4	13.7	80.9	50.0	97.2	A−B
R	Available PPP	%TPP	69.4	13.9	74.0	40.0	95.2	Q−E
S	BP	%TPP	12.1	7.8	11.1	1.0	41.8	g_0×D
T	Bacterial lysis by viruses	%TPP	3.0	0.2	2.7	0.2	12.0	S×P
U	Micro-Z ingestion	%TPP	52.4	10.9	52.5	21.7	89.1	(F×H)+(S−T)
V	Micro-Z assimilation	%TPP	36.7	7.6	36.7	15.2	62.4	U×I
W	Micro-Z biomass	%TPP	16.3	5.2	15.8	3.1	42.3	$U\times\overline{(J,K,L)}$
X	Micro-Z egestion of DOC	%TPP	7.9	1.6	7.9	3.2	13.3	(V−U)×H
Y	Micro-Z excretion	%TPP	6.3	1.3	6.3	2.6	10.7	U×O
Z	Meso-Z grazing	%TPP	36.8	9.3	36.2	11.8	72.5	R−(F×R)+(W×M)
a	Meso-Z sloppy feeding	%TPP	5.4	3.5	5.1	0.0	20.1	Z×G

(Continues)

Table 1. Continued

Derived parameters		Basis	Mean	SD	Median	Min	Max	Calculation
b	Meso-Z ingestion	%TPP	31.3	8.5	30.7	9.7	70.8	Z−a
c	Meso-Z assimilation	%TPP	21.9	6.0	21.5	6.8	49.6	b×I
d	Meso-Z biomass	%TPP	8.7	5.3	8.1	0.1	34.4	b×N
e	Meso-Z egestion of DOC	%TPP	4.7	1.3	4.6	1.5	10.6	(b−c)×H
f	Meso-Z excretion	%TPP	3.8	1.0	3.7	1.2	8.5	b×O

Results		Basis	Mean	SD	Median	Min	Max	Calculation
g	ΣSources	%TPP	61.6	11.1	60.4	33.2	101.4	B+E+T+X+Y+a+e+f
	Demand	%TPP	52.0					C×(1−B)/D

viruses, they route carbon away from POC that might otherwise be transferred to higher trophic levels or exported. In fact, one estimate reported that 50–70% of host biomass is made available for bacterial remineralization during Syndiniales infections of the dinoflagellate *Akashiwo sanguinea* (Yih and Coats 2000). Parasitic chytrid fungi, also newly recognized as abundant members of ocean microbial communities, may decrease phytoplankton DOC release by directing carbon into fungal biomass (Klawonn et al. 2021). Quantification of marine protist and fungal parasite contributions to the labile DOC pool awaits a better understanding of their basic ecological dynamics (e.g., infection patterns, host preferences; Anderson and Harvey 2020) and field methodology to tease apart parasite-released DOC from that of other sources.

Finally, organic matter release from phytoplankton cells occurs during senescence, for instance during the demise of a bloom. Quantitative data on this process are also limited, in part because of the multiple mechanisms of cell mortality, for example "programmed cell death" (Berges and Falkowski 1998; Vardi et al. 1999; Berman-Frank et al. 2004; Franklin et al. 2006) and microbial algicides (Paul and Pohnert 2011; van Tol et al. 2017; Legrand et al. 2019), and in part because of the limited techniques to directly measure phytoplankton senescence. Metabolic indicators of stress such as protease synthesis, DNA fragmentation (Franklin et al. 2006), and extracellular release of internal phytoplankton enzymes such as esterases (van Boekel et al. 1992; Brussaard et al. 1995; Agustí et al. 1998; Agustí and Duarte 2000) have been used as markers of dying and ruptured phytoplankton. The latter method shows high cell mortality in pelagic marine systems that is distinct from that caused by zooplankton grazing and physical removal; an example being 75% of phytoplankton loss during the decline of a North Sea *Phaeocystis* bloom (Brussaard et al. 1995). Yet, death due to senescence is also problematic to distinguish from other mortality mechanisms that release phytoplankton cell contents into seawater, such as viral infection, sloppy feeding, and parasitic infection. Data were too few to explicitly include senescence in source estimates, but DOC generated from nonpredatory phytoplankton death may be partially accounted for in methods intending to quantify contributions from infection or predation (Fig. 3).

Input 3: Labile DOC from heterotrophs

Zooplankton and bacteria release labile DOC in the form of secondary production when assimilated carbon is excreted as waste. Saba et al. (2011) found that a copepod excreted 12% of carbon ingested, with the remaining going to respiration, growth, egg production, and sloppy feeding. In addition to phytoplankton prey, zooplankton also graze within the zooplankton community. Mesozooplankton consumption of microzooplankton is estimated to range from 30% to 100% of microzooplankton production; the lower end is calculated based on two trophic transfers within the zooplankton and the higher end is based on one (Steinberg and Landry 2017) (Supporting Information Fig. S1). We parameterized the model with the single value of 12% for excretion losses when mesozooplankton feed on either phytoplankton or smaller zooplankton (Table 1). Uncertainty in the parameter is associated with sampling techniques that exclude small copepods (Turner 2004), overrepresentation of coastal areas in data gathering (Schmoker et al. 2013), complexity imposed by diel migration (Calbet 2001; Schmoker et al. 2013; Steinberg and Landry 2017), and the uncertainties regarding the number of trophic transfers occurring within the zooplankton community. For the gelatinous mesozooplankton that bloom in coastal waters, such as jelly fish, ctenophores, and planktonic tunicates (Deibel 1988; Paffenhöfer et al. 1995; Walters et al. 2019; Ishak et al. 2020), damage during sampling is common (Hosia et al. 2017; Long et al. 2020) and likely leads to an underestimate of their contributions to grazing and thus their role in labile DOC release.

As was the case for phytoplankton, viral infection is also a source of labile DOC from heterotrophic members of the microbial food web. Infection and lysis of microzooplankton by natural viral communities has been observed in the laboratory (Garza and Suttle 1995) and is expected to occur in the

ocean, although the carbon released by this process has not been directly measured. Due to lack of data, labile DOC release from zooplankton infection could not be explicitly included in the model. In the case of heterotrophic bacteria, infection and lysis by viruses can redirect ~ 75% of host organic matter into virions. Following lysis, the DOC released from the host cell can then be taken up by uninfected bacteria (Ankrah et al. 2014). To parameterize bacterial lysis, we again relied on the virus model of Wilhelm and Suttle (1999) which estimates that 20–30% of BP passes through the viral shunt to the labile DOC pool (Fig. 3; Table 1). Healthy marine bacteria also directly release organic molecules into seawater as they grow (Kujawinski et al. 2009; Wienhausen et al. 2017), and these compounds can be assimilated by neighboring bacteria (Ortega-Retuerta et al. 2020). However, quantitative data on bacterial release are lacking and therefore also not included here.

Supply-based estimate

A steady state flow analysis was generated to integrate estimates of these multiple sources of bioavailable dissolved molecules (github.com/wschroer/labile_DOC_supply_chain; Supporting Information Fig. S1). The model distributed TPP among organic matter stocks according to 16 primary parameters and 16 derived parameters (given in Table 1 and explained in the text below). Except for the four parameters constrained to a single value, the model randomly selected primary parameter values at each iteration by resampling from values reported in the literature or by random draw from an assumed distribution (Table 1), depending on the sparseness of experimental data. Once in the surface ocean labile DOC pool, carbon is taken up by heterotrophic bacteria and a fraction converted back into labile DOC during another turn of the microbial loop; the same carbon atom can thereby cycle through the DOC pool more than once (Anderson and Ducklow 2001). To account for this, each model run included a second circuit in which labile DOC generated in the first circuit was processed through the heterotroph portion of the model using the same parameter values (Supporting Information Fig. S1, blue shading); while this loop could be repeated indefinitely on a diminishing pool of labile DOC, the single recycling circuit used here added 4 Pg C yr^{-1} (equivalent to 6.1% of TPP; Fig. 3b) to the labile DOC pool, while five circuits would have generated only an additional 0.7 Pg C yr^{-1}. Labile DOC generated in the first (full model) and second (recycling) circuits was summed for each iteration in the run, and means and standard deviations were calculated after 100,000 runs.

Model output estimated an annual influx to the labile DOC pool of 39 Pg C yr^{-1} (Fig. 3), an amount equivalent to 62% of TPP. Among the three major sources, the fraction of labile DOC generated through (1) direct release from healthy phytoplankton was 0.4; (2) release from dead and dying phytoplankton (viral lysis, sloppy feeding, egestion) was 0.4; and (3) release of heterotrophic carbon (excretion and viral lysis) was 0.2 (13% of TPP).

Demand-based estimate

The second analysis approach addressed the quantitative role of labile DOC using a top-down strategy based on the amount of carbon required to support bacterial production plus respiration (BP + BR). We leveraged a method used by Cole et al. (1988) which systematically gathered data on the relationship between BP and PP. The demand calculation does not require knowledge of sources, but instead uses measures of bulk carbon flux into bacterioplankton cells as a proxy for labile DOC availability. However, it assumes that utilization of labile compounds dominates bacterial uptake measurements; this is correct to the extent that particle-associated bacteria liberate organic matter into dissolved form prior to assimilation, and that refractory DOC uptake is a negligible component of total DOC uptake.

We examined relevant literature published after 1988 using the same criteria for data selection and unit conversion as Cole et al. (1988), and identified 28 post-1988 studies reporting both PPP and BP in marine photic zones (Supplementary Table S2). The PPP and BP values in these more recent studies are within the ranges reported in Cole et al. (1988) (10^0–10^3 mg C m^{-3} d^{-1} for primary production and 10^{-1}–10^2 mg C m^{-3} d^{-1} for BP; Supplementary Table S2). BP is equivalent to an average of 13% of PPP in our survey of recent literature, close to the 17% value for pelagic marine environments compiled by Cole et al. (1988) (Fig. 2b), with a mean value for pre- and post-1988 studies of 15% of PPP (Table 1). An analysis carried out by Fouilland and Mostajir (2010) that included hundreds of measurements from the Joint Global Ocean Flux Study, Bermuda Atlantic Time-Series, and other time series programs estimated the median BP in ocean waters to be equivalent to 15% of PPP (our median, 10%).

BR generates energy for cells through catabolism of organic carbon. The total carbon needed to support heterotrophic bacteria (the bacterial carbon demand [BCD]; Box 1) is therefore the sum of BP and BR (del Giorgio and Cole 2000):

$$\mathrm{BCD} = \mathrm{BP} + \mathrm{BR}$$

Studies that reported simultaneous measures of BP and BR generated estimates of BGE (Table 1) as:

$$\mathrm{BGE} = \frac{\mathrm{BP}}{\mathrm{BP} + \mathrm{BR}}$$

Early measurements of BGE typically ranged from 40% to 60% (Crawford et al. 1974; Cole et al. 1982; Joint and Morris 1982) and reached values > 60% in assays with simple substrates such as glucose and amino acids (Hobbie and Crawford 1969). These studies initially led to parameterization of BGE at 50%

(Cole et al. 1988; Lignell 1990; Baines and Pace 1991), but this was subsequently modified downward based on data from natural environments in the range of 10–30% (Bjørnsen 1986; Kroer 1993; Pomeroy et al. 1995; Carlson and Ducklow 1996). In 1998, del Giorgio and Cole (1998) analyzed published measurements of BGE and calculated mean values of 23% and 34%, respectively, for ocean and estuarine systems, although with substantial interstudy variability. For the purposes of this analysis, we surveyed literature published after 1998 (Supplementary Table S3) and obtained an average BGE of 11% in oceanic regions and 24% in estuaries from nine studies, with a similarly wide range across studies (Fig. 2c). Such variability across BGE measurements has prompted suggestions that growth efficiency be calculated independently in each system, with no "universal" value applied (Kroer 1993; Pomeroy et al. 1995; Carlson and Ducklow 1996). In our demand calculation, the mean value of published BGE measurements of 0.22 was used (Fig. 2c) and the total demand for carbon to support bacterial requirements was determined as:

$$\mathrm{BCD} = \frac{\mathrm{BP}}{\mathrm{BGE}}$$

The resulting demand-based estimate for annual flux into the labile DOC pool is 33 Pg C yr^{-1}, compared to 39 Pg C yr^{-1} predicted in the ΣSources model. The two approaches are not independent, however, as they share the %ER and BGE parameters (Table 1).

Knowledge gaps

Many of the parameters used in our estimates have either been sparsely measured or poorly constrained. For three parameters for which ample literature data are available ($n \geq 30$), the difference between minimum and maximum reported values is 18-fold (DPP as a percent of TPP), 88-fold (BP as a percent of PPP), and 18-fold (BGE) (Table 1). These ranges likely reflect the use of different methodologies, but also represent true variation across space and time due to factors in the local environment such as species composition, nutrient and temperature regimes, number of trophic transfers within the microbial food web, and cell stress. Except for grazing rates on phytoplankton (Schmoker et al. 2013), parameters capturing zooplankton activities are among the most sparse and are focused on a limited number of taxa, primarily copepods, and ciliates. Moreover, the mechanisms by which zooplankton release DOC during grazing (sloppy feeding, viral lysis, parasitic lysis, senescence, egestion, and excretion) are particularly difficult to separate experimentally. Finally, recent evidence suggests that microbes other than bacteria can assimilate carbon directly from the labile DOC pool, including archaea (Orellana et al. 2019; Tully 2019), fungi (Baltar et al. 2021), and heterotrophic flagellates (Sherr 1988). However, these groups are likely to be minor players in surface ocean DOC uptake compared to heterotrophic bacteria.

Some potential sources of labile DOC could not be considered in the ΣSources model because direct measures are not yet available. Examples include inputs from phytoplankton senescence, fungal parasitism, and viral lysis of zooplankton, although current methodologies may bundle some of these mechanisms together. Mixotrophy exists in the microbial ocean in the form of heterotrophic feeding by autotrophs and in the form of autotrophic carbon or energy acquisition by heterotrophs (Stoecker et al. 2017; Godrijan et al. 2020). From a conceptual standpoint, we do not expect most mixotrophic activity to substantially alter model predictions because many studies capture autotrophic and heterotrophic activities regardless of how they are partitioned into individual cells. In the case of bacterial mixotrophy, energy transduction by proteorhodopsin or bacteriochlorophyll (Moran and Miller 2007) could sustain some portion of basal metabolic costs (Gómez-Consarnau et al. 2019), and thus increase BGE by routing more carbon to biomass. Yet, because the models are based on experimentally measured BGE values that simply tally carbon fate, we expect this alternate energy source will not substantially impact model results. Finally, episodic events such as storms and physical mixing can influence primary production, phytoplankton mortality, and microbial community composition (Johnson et al. 2010; Garrison and Tang 2014; Avila-Alonso et al. 2021; Rii et al. 2021; Wang and Zhang 2021). While planktonic communities often return to pre-event status within days or weeks (Rii et al. 2021), episodic events may have significant local implications for DOC flux and fate, and these were not captured in the data used here.

Synthesis

Measurements generated over several decades of microbial and chemical research were used to build an updated perspective on the role of labile DOC in the surface ocean. One analytical approach used a bottom-up strategy that merged measures of metabolite release from trophic groups within the microbial food web (ΣSources model). This model hypothesizes that carbon from primary production (i.e., derived from living and dead/dying phytoplankton) accounts for 80% of labile DOC inputs, while carbon from secondary production (i.e., derived after trophic transfer to heterotrophs) accounts for 20% (Fig. 3). However, the activities of heterotrophs are required for generating 50% of labile DOC because of the importance of zooplankton release of phytoplankton carbon during grazing but prior to assimilation (sloppy feeding and egestion). In a sensitivity analysis of model parameters, the proportion of TPP released by living phytoplankton (the %ER parameter) had the largest influence over model output, accounting for 77% of the variation between runs (Supporting Information Fig. S2); no other parameter predicted more than 5% of between-run variance. DPP is the most direct source of

metabolites to the labile DOC pool, and in our model it also sets the fraction of TPP remaining as particulate material (the PPP parameter). Phytoplankton senescence and viral lysis also represent direct mechanisms that transfer phytoplankton-derived molecules into labile DOC, but the former is not represented in the model due to lack of data (although it may already be bundled into other measures, such as DPP), and the latter accounts for ≤ 8% of labile DOC inputs.

To address a possible point of confusion, we note that these two calculations estimate the *amount of labile DOC available for bacterial processing*, some of which enters the DOC pool only once (90% based on the first circuit through the ΣSources model) and some of which enters more than once (10% based on the recycling circuit). Thus, they do not represent the *fraction of fixed carbon atoms that pass through the labile DOC pool*. To estimate the latter, we ran the ΣSources model with only the first circuit operating, leaving out recycling of labile DOC. In this case, the model estimates that 55% of fixed carbon atoms reside at least once in the labile DOC pool.

We compared these results to earlier studies. Cole et al. (1988) estimated that BP averaged 20% of PPP, similar to the ΣSources model in which BP averaged 16% of PPP. Baines and Pace (1991) predicted that 32% of BCD is derived from extracellular release by living phytoplankton, and our ΣSources model estimate is similar at 40% (24.5/61.5 = 0.40; Table 1). The Anderson and Ducklow (2001) model of carbon flux through the microbial loop concluded that zooplankton release is a major mechanism by which marine bacteria access labile DOC; our model agrees, predicting zooplankton to be responsible for ~ 50% of labile DOC, considering contributions from both phytoplankton-derived metabolites liberated through zooplankton grazing and from heterotroph-derived metabolites liberated through zooplankton and bacterial waste and lysis products.

This new analysis of an old question similarly concludes that approximately half of newly fixed marine carbon passes through the labile DOC pool and is rapidly transformed by bacteria. While noting the high variability in parameter ranges, much of it likely real biological variation over space and time, we conclude that all three major sources contribute substantially to labile DOC, and hypothesize a 0.4 fractional contribution each from living and dead/dying phytoplankton carbon, and a 0.2 contribution from heterotroph carbon. The fact that the percent of TPP routed to extracellular release by living phytoplankton was a highly influential parameter in our estimates, yet has a very wide range in reported values, suggests that more and better data on this specific process may be a strategic approach to constraining predictive uncertainty. Changes in the microbial partitioning of labile DOC between bacterial biomass production and respiration, that is, the BGE parameter, could be affected by future shifts in marine metabolite sources, microbial taxonomy, and nutrient limitation, and have the potential to alter the fate of a significant annual flux of carbon. A better understanding of the factors that govern the sources and composition of labile DOC in a changing ocean is clearly warranted.

Data Availability Statement

Model code is available at github.com/wschroer/labile_DOC_supply_chain. Data and source publications for literature surveys are provided in Supplementary Tables S1–S3.

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Conflict of Interest

None declared.

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