Variable ageing and storage of dissolved organic components in the open ocean

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Seawater dissolved organic matter (DOM) is the largest reservoir of exchangeable organic carbon in the ocean, comparable in quantity to atmospheric carbon dioxide\(^1,2\). The composition, turnover times and fate of all but a few planktonic constituents of this material are, however, largely unknown\(^3,4\). Models of ocean carbon cycling are thus limited by the need for information on temporal scales of carbon storage in DOM subcomponents, produced via the ‘biological pump’, relative to their recycling by bacteria\(^5,6\). Here we show that carbohydrate- and protein-like substances in the open Atlantic and Pacific oceans, though often significantly aged, comprise younger fractions of the DOM, whereas dissolved lipophilic material exhibits up to ~90 per cent fossil character. In contrast to the millennial mean ages of DOM observed throughout the water column, weighted mean turnover times of this DOM in the surface ocean are only decadal in magnitude. An observed size–age continuum further demonstrates that small dissolved molecules are the most highly aged forms of organic matter, cycling much more slowly than larger, younger dissolved and particulate precursors, and directly links oceanic organic matter age and size with reactivity\(^5,6\).

Seawater DOM consists of analytically identifiable biochemicals such as carbohydrates, proteins and lipids, as well as operationally defined and long-lived geomacromolecules (for example, humic and fulvic substances\(^6,7\)). In order to resolve some of the key details of DOM sources and cycling in the oceans, major organic components were extracted from high-molecular-weight ultrafiltered DOM\(^8\) (DOM\(_{HMW}\) > 1,000 daltons) collected from 1,000–3,000 m of sea water, and analysed for both \(^{13}\)C and \(^{14}\)C isotopic signatures. Samples were collected from surface mixed-layer (3–20 m), mesopelagic oxygen-minimum (850–900 m), and abyssal (1,500–1,800 m) depths in the central North Pacific (June 1999) and the Sargasso Sea region of the North Atlantic (June 2000) oligotrophic ocean gyres. The contributions of soluble-extractable lipids, protein-like and carbohydrate-like organic matter (OM), as well as different molecular-weight fractions, to the overall age structure of seawater DOM, were thus established.

By far the most highly aged DOM component was the lipid extract (6.4–17.1 kyr before present, BP; Table 1), with \(^{14}\)C ages in the deep Pacific representing the greatest yet observed for any component of seawater OM. The lipid extract was considerably older by ~5–13 kyr than the total DOM\(_{HMW}\) and unfractinated, bulk DOM (ΣDOM) pools (Tables 1 and 2; Fig. 1a). Furthermore, at all mesopelagic and abyssal depths, the lipid extract and DOM\(_{HMW}\) were older in the Pacific than in the Atlantic, similar to the ocean–ocean offsets observed for ΣDOM\(^6\) (Table 1) and presumably due to cumulative ageing during deep water-mass transit\(^8\). Conversely, mixed-layer lipid extract, DOM\(_{HMW}\) and ΣDOM were all older in the Atlantic than in the Pacific (Tables 1 and 2), suggesting possible aged North American continental or atmospheric inputs there\(^7\). The highly \(^{13}\)C-depleted signatures of lipid extracts (Table 1, Fig. 1b) are consistent with isotopic fractionations during cellular lipid...
synthesis\(^{16}\). Thus, these fossil dissolved lipids arise either from extensive ageing within the oceans, with concomitant recycling over many ocean circulation times\(^{4}\), or from inputs of one or more pre-aged lipophilic precursors\(^{7}\). Concurrent elemental ratios (Table 2) and lipid biomarker data\(^{12}\) of total DOM\(_{HMW}\) suggest, however, that the lipid extract may be dominated by planktonic, rather than petrogenic, material.

Dissolved protein-like and carbohydrate-like fractions were similar in \(^{14}C\) age, ranging from modern to \(\sim 3\)–4 kyr BP (Table 1). Modern to near-modern ages in surface waters indicate that both fractions are derived from recent, post-bomb (that is, after 1955) marine production, and contain little aged or recycled material. In deeper waters, however, these components, which are quite reactive in surface waters\(^8\), are deduced to have escaped degradation over many ocean circulation times\(^2\) and to have aged extensively. The protein- and carbohydrate-like components were younger by as much as \(\sim 13\)–14 kyr compared to the corresponding lipid extract (Table 1), and by as much as \(\sim 1\) kyr (Fig. 1a) compared to DOM\(_{HMW}\) supporting the contention that ‘old’ seawater \(\Sigma\)DOM\(_{HMW}\) is actually composed of components having a spectrum of ages and reactivities. Transport-based ageing of protein- and carbohydrate-like DOM is also suggested at mesopelagic and abyssal depths (Table 1), similar to the \(\Sigma\)DOM\(_{LMW}\), total DOM\(_{HMW}\) and lipid extract (Tables 1 and 2).

Dissolved forms of all three major organic fractions were significantly older than their particulate counterparts\(^{13,14}\) (Fig. 2). Dissolved lipid extracts were \(\sim 6\)–17 kyr older than lipid extracts of sinking particulate OM (POM; 3,500 m depth)\(^{13,14}\), suggesting that dissolved and particulate lipids cycle on dramatically different timescales or arise from dissimilar sources. The latter possibility is supported by correspondingly lower \(^{13}C\) of dissolved lipids (about \(-29\) to \(-28\%\)o; Table 1) compared to particulate and sedimentary lipids (\(-25\)% to \(-22\%\)o; refs 13, 14; Fig. 2). Additionally, particulate lipids may contain both a highly aged component, similar to the dissolved pool, and a recently derived component from contemporaneous marine production\(^8\), accounting for their intermediate ages. Deep dissolved protein- and carbohydrate-like fractions were also significantly older by \(\sim 3\)–4 kyr than particulate forms\(^3,13,14\), whereas the relative abundances of these two fractions are reversed in the dissolved (Table 1) compared to particulate phases\(^3,13,14\), suggesting dissimilar sources or preservation. Therefore, although the dissolved fractions are far more abundant, they are also far longer-lived.

### Table 1 Isotopic signatures of organic fractions contained in seawater DOM\(_{HMW}\)

| Depth  | LE  | CL  | MUC |
|--------|-----|-----|-----|
| %*     | \(\Delta^{13}C(\%)\) | %* | \(\Delta^{13}C(\%)\) | %* | \(\Delta^{13}C(\%)\) |
| Atlantic |     |     |     |     |     |     |
| 3 m    | 0.1 | -637 | -281 | 13.3 | 2 | -21.2 | 47.5 | 13 | -21.5 | 39.1 | -28 | -22.3 |
| 850 m  | 0.3 | -730 | -281 | 17.1 | -190 | -20.4 | 38.9 | -228 | -20.4 | 43.7 | -336 | -21.7 |
| 1,500 m| 0.2 | -830 | -281 | 22.9 | -215 | -20.8 | 33.8 | -309 | -211 | 43.0 | -246 | -21.5 |
| Pacific |     |     |     |     |     |     |     |     |     |     |     |     |
| 20 m   | 0.3 | -551 | -27.6 | 19.0 | -21 | -211 | 35.9 | 7 | -21.4 | 44.9 | -199 | -22.3 |
| 900 m  | 0.3 | -864 | -29.4 | 15.4 | -279 | -21.0 | 27.7 | -302 | -20.4 | 56.7 | -444 | -22.1 |
| 1,800 m| 0.3 | -881 | -29.4 | 16.9 | -332 | -20.8 | 41.1 | -406 | -20.3 | 41.7 | -499 | -22.3 |

*% of each organic fraction in DOM\(_{HMW}\), based on C equivalents measured after combustion to CO\(_2\).
†MUC = \(100 - (\%LE + \%PL + \%CL)\). Isotopic signatures of MUC were estimated by isotopic mass balance, as: \(X_{PL} = X_{DOM} - f_{DOM}X_LE - f_{DOM}X_CL\), where \(X\) is the \(\Delta^{13}C\) or \(\delta^{13}C\) signature of each organic fraction, \(f_{DOM}\) is the relative contribution of each to the total DOM\(_{HMW}\) pool, and \(f_{DOM} + f_{LE} + f_{CL} + f_{MUC} = 1.0\).
‡Assumed from average of all observed values in that group for purposes of inclusion of \(\Delta^{14}C\) or \(\delta^{14}C\) in Fig. 2.
§Values in parentheses are \(\Delta^{14}C\) ages in yr BP calculated from \(\Delta^{14}C\) values as: \(yrBP = -8,634 (1 + \Delta^{14}C/13\)‰\). Where yr BP indicate years before 1950, prior to thermonuclear weapons testing
\[\Delta^{14}C\] values were not reservoir-corrected, all ages are not true calendar ages.

### Table 2 Isotopic and elemental characteristics of seawater DOM size classes

| Depth  | \(\Delta^{13}C(\%)\) | \(\delta^{13}C(\%)\) | \(\Delta^{14}C(\%)\) | \(\delta^{14}C(\%)\) | C:N | C:P | N:P |
|--------|------------------|------------------|------------------|------------------|-----|-----|-----|
| Atlantic |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 3 m    | -238 | -21.3 | -5 | -21.8 | -280 | -21.2 | 14 | 353 | 25 |
| 850 m  | -375 | -21.2 | -270 | -21 | 383 | -21.2 | 14 | 268 | 19 |
| 1,500 m| -378 | -20.8 | -262 | -21.2 | 384 | -20.8 | 14 | 196 | 14 |
| Pacific |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 20 m   | -191 | -21.2 | -92 | -21.8 | -210 | -21.1 | 15 | 280 | 19 |
| 900 m  | -470 | -20.8 | -381 | -21.5 | -481 | -20.7 | 14 | 284 | 21 |
| 1,800 m| -533 | -21.2 | -434 | -21.3 | -539 | -21.2 | 14 | 256 | 18 |

\*Unfractionated, bulk DOM values\(^{15}\).
†High-molecular-weight DOM was 15–16% of ZDOM in surface waters, and 5–11% in deeper waters based on C recoveries after ultrafiltration, diaphragmation and lyophilisation. These recoveries are consistent with the range of recoveries reported in other studies\(^{15}\).
‡Isotopic signatures of low-molecular-weight DOM, estimated by isotopic mass balance as: \(X_{DOM} = X_{ZDOM} - f_{DOM}X_{HMW}/(1 - f_{HMW})\), where \(X\) is the \(\Delta^{13}C\) or \(\delta^{13}C\) value of each molecular weight fraction, \(f_{DOM}\) is the relative contribution of each to the total DOM\(_{HMW}\) pool, and \(f_{DOM} + f_{HMW} = 1.0\).
§Values in parentheses are \(\Delta^{14}C\) ages in yr BP calculated from \(\Delta^{14}C\) values as in Table 1.
||\(\Delta^{14}C\) and \(\delta^{14}C\) pair in Fig. 2.\|
and are thus deduced to be less reactive to bacteria than the younger particulate fractions. Dissolved carbohydrates have further been found to contain specific sugars of modern 14C age16, indicating that even within a given organic fraction individual molecules may have unique cycling times, similar to findings for individual sedimentary lipids17.

The highly modified, acid-insoluble fraction of DOM_{HMW} (analogous to the molecularly uncharacterized, MUC, component of OM14) was estimated to comprise 39–57% of DOM_{HMW} carbon (Table 1). These large amounts of MUC-like DOM and its estimated ages (0.2–5.6 kyr BP; Table 1) suggest that much of the ΣDOM is composed of structurally modified biopolymers and geomolecules17, probably derived from combinations of diagenetically altered younger proteins and sugars and older lipid components. Based on their disparate Δ14C and δ13C signatures (Table 1, Fig. 2), however, the dissolved forms of MUC and lipid extract are unlikely to share a common origin as has been suggested for POM14. Instead, dissolved MUC in deep waters is isotopically more similar to, and thus may arise from, dissolved protein- and carbohydrate-like and humic materials6 (Fig. 2), or from a precursor common to each. This is further supported by NMR studies demonstrating that DOM_{HMW} contains significant acyl polysaccharide, a carbohydrate-derived biopolymer6.

Radiocarbon ages for total DOM_{HMW} ranged widely, from modern to 4.6 kyr BP (Table 2), and were younger than ΣDOM1,6 (Table 1). These large amounts of MUC-like DOM and its estimated ages (0.2–5.6 kyr BP; Table 1) suggest that much of the ΣDOM is composed of structurally modified biopolymers and geomolecules17, probably derived from combinations of diagenetically altered younger proteins and sugars and older lipid components. Based on their disparate Δ14C and δ13C signatures (Table 1, Fig. 2), however, the dissolved forms of MUC and lipid extract are unlikely to share a common origin as has been suggested for POM14. Instead, dissolved MUC in deep waters is isotopically more similar to, and thus may arise from, dissolved protein- and carbohydrate-like and humic materials6 (Fig. 2), or from a precursor common to each. This is further supported by NMR studies demonstrating that DOM_{HMW} contains significant acyl polysaccharide, a carbohydrate-derived biopolymer6.

Radio carbon ages for total DOM_{HMW} ranged widely, from modern to 4.6 kyr BP (Table 2), and were younger than ΣDOM1,6 from the Atlantic and Pacific (Table 2). Therefore, ΣDOM must by definition also contain an older, low-molecular-weight (LMW) component in order to balance the younger DOM_{HMW} (ref. 19; Table 2). In addition to being the oldest size fraction yet identified for seawater OM (~1.9–6.2 kyr BP), DOM_{LMW} is also the most abundant, comprising 77–95% of EDOM. The δ13C signatures of this older LMW material further suggest that it arises directly from recycling of younger DOM_{HMW} (Table 2). Observations of old DOM_{LMW} intermediate-aged DOM_{HMW} and young POM14–19 in the oceans reveal a pronounced size–age relationship among the major forms of seawater OM (Table 2; Fig. 2). The two main forms of POM (that is, sinking and suspended) consistently contain bomb 14C (Δ14C range: about −100‰ to +160‰ for suspended POM, and about −30‰ to +35‰ for sinking POM) throughout the Pacific and Atlantic water columns12,19. However, only surface DOM_{HMW} is similarly enriched, while LMW material contains no apparent bomb 14C at any depth (Table 2; Fig. 2). That is, 14C age increases consistently in the size sequence from sinking POM (the youngest, largest fraction), to suspended POM, to DOM_{HMW} and finally DOM_{LMW} (the oldest, smallest fraction; Fig. 2), and most probably arises from sequential hydrolysis, dissolution and/or degradation of larger forms of OM to successively smaller fractions. This also suggests that the relative rate of OM respiration slows as highly aged LMW material accumulates in the latter stages of degradation.

An important corollary of this size–age continuum is that it coincides with a previously observed OM size–reactivity continuum2,3, ranging from structurally complex and recently produced sinking POM and DOM_{HMW} (most reactive to bacterial degradation) to structurally simple but highly reworked DOM_{LMW} (least reactive to bacterial degradation). The proposed size–age model for seawater OM is therefore consistent with higher utilization rates of DOM_{HMW} than DOM_{LMW} in oceanic and coastal waters6,5 as well as with the presence of younger, presumably more reactive sub-components3,16 in DOM_{HMW} (Fig. 1a). Studies of EDOM degradation further support the presence of specific bioavailable subfractions of this large, heterogeneous pool. Besides the 14C evidence, highly elevated elemental ratios of DOM_{HMW} (Table 2; ref. 21) compared to recently produced ‘Redfield’ OM (C:N:P ≈ 106:16:1), together with the presence of bacterial fatty acids in oceanic DOM_{HMW} (ref. 12), further support the contention that dissolved components may have undergone extensive recycling compared to POM (Fig. 2). An alternative to the proposed size-dependent ageing model for seawater OM is that there exist one or more structurally similar sub-fractions, each of which resides in a different size fraction, and which are all derived from the same precursor. Figure 1. Isotopic signatures of dissolved organic fractions relative to DOM_{HMW}. a. Plotted for Δ14C (as Delta Δ14C); and b. plotted for δ13C (as Delta δ13C) for three depths each in the Sargasso Sea region of the North Atlantic and in the central North Pacific. LE, lipid-extract fraction; PL, protein-like fraction; CL, carbohydrate-like fraction; MUC, molecularly uncharacterized fraction. See Table 1 for assumed δ13C values.

**Figure 2** Δ14C versus δ13C for dissolved organic fractions, DOM_{HMW}, and DOM_{LMW}. Data from the present study are plotted as discrete points, along with ranges for potential sources of DOM in the North Atlantic and North Pacific oceans (boxes) compiled from the literature as follows: sinking POM17, suspended POM; bulk DOM12; dissolved humic substances; Sahara dust bulk organic matter and black carbon fraction; urban aerosol19, North Pacific and Southern Ocean sedimentary black carbon22; and petroleum29. Shaded boxes show Δ14C and δ13C ranges for organic fractions isolated from sinking POM12,14. Abbreviations as in Fig. 1. See Tables 1 and 2 for assumed δ13C values.
more allochthonous or autochthonous sources of pre-aged DOM in the oceans that are largely independent of plankton-dominated OM formation and degradation. While aged allochthonous sources of DOM such as submicrometre fossil black carbon are probably minimal on the basis of the observed OM size–age distributions (Fig. 2), other ‘pre-aged’ inputs may include natural hydrocarbon seepage in certain ocean regions and atmospheric deposition. Soluble forms of seawater OM are further predicted to escape degradation and undergo ageing either within the deep ocean, or during surface–deep ocean transport, by mechanisms different from those such as sorptive preservation identified for particulate and sedimentary forms.

Within the oceanic DOM pool, various organic and size fractions persist on radically different timescales (Tables 1 and 2). The turnover time (TOT) of undifferentiated bulk pools such as DOM is equivalent to its 14C age if substances in the bulk pool are uniform in age. However, the presence of discrete organic and size fractions having different 14C ages (and therefore different rates of turnover) results in a weighted mean TOT that departs from the dominance of the SOM mass of the organic and size fraction ages (Tables 1 and 2), the weighted mean TOT for surface ocean DOM is estimated to be ~60–90 yr, increasing to ~3,700–6,000 yr in Atlantic and Pacific deep waters, respectively (see Supplementary Table S1). Surface ocean differences between the weighted mean TOT (decadal) and DOM 14C ages (millennial) result from surface DOM being dominated by young protein- and carbohydrate-like fractions that are recycled rapidly compared to the balance of the DOM. This contrasts with deep waters, where DOM ages and TOT converge owing to the uniform low reactivity and turnover of all subcomponents.

Methods

Sample collection and organic fraction separation

Large-volume (1,000–3,000 l) water samples were collected using 30-l rosette-mounted Niskin bottles. Samples were pre-filtered (0.2-µm) and transferred to an Amicon DC-10L tangential flow ultrafiltration system equipped with spiral wound filter cartridges with a 1,000 dalton molecular-weight cut-off. Samples were reduced to ~11 and frozen until processing. For analyses, samples were thawed, dialysed to remove salts, and lyophilised, followed by sequential extraction for solvent-extractable lipids, protein-like and carbohydrate-like organic fractions. Total lipids were extracted from the lyophilised sample using a modified Bligh-Dyer extraction with dichloromethane-methanol (2:1 v/v) and a Dionex accelerated solvent extractor. Residue from the lipid extraction was divided followed by sequential extraction for solvent-extractable lipids, protein-like and carbohydrate-like organic subcomponents (lipid extract, protein-like, carbohydrate-like and MAC fractions) and DOM$_{Lipid}$ as:

$$k_i = \frac{F_i}{\Delta C}$$

where $k_i$ is the turnover rate constant in yr$^{-1}$ for fraction $i$, $F_i$ is the relative contribution of fraction $i$ to the DOM pool, and $\Delta C$ is the 14C age of fraction $i$ (Tables 1 and 2, Supplementary Table S1). The weighted mean TOT of DOM is then calculated as:

$$\text{TOT}_{DOM} = \frac{1}{S} \sum_i k_i$$

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1. Williams, P. M. & Druffel, E. R. M. Radiocarbon in dissolved organic carbon in the central North Pacific Ocean. Nature 330, 246–248 (1987).
2. Hedges, J. I. Global biogeochemical cycles: progress and problems. Mar. Chem. 39, 67–93 (1992).
3. Amon, R. W. M. & Benner, R. Bacterial utilization of different size classes of dissolved organic matter. Limnol. Oceanogr. 41, 41–51 (1996).
4. Carlson, C. A. in Biogeochemistry of Marine Dissolved Organic Matter (eds Hansell, D. A. & Carlson, C. A.) 91–131 (Academic, Orlando, USA, 2002).
5. Benner, R. in Biogeochemistry of Marine Dissolved Organic Matter (eds Hansell, D. A. & Carlson, C. A.) 59–90 (Academic, Orlando, USA, 2002).
6. Bauer, J. E., Williams, P. M. & Druffel, E. R. M. 14C activity of dissolved organic carbon fractions in the north central Pacific and Sargasso Sea. Nature 357, 667–670 (1992).
7. Druffel, E. R. M., Bauer, J. E. & B. M. Cycling of dissolved and particulate organic carbon in the open ocean. J. Geophys. Res. 97, 15639–15659 (1992).
8. Suiker, M., Quay, P. D. & Outland, H. L. Abyssal water 14C distribution and the age of the world oceans. Science 238, 849–851 (1987).
9. Eglinston, T. J. et al Composition, age, and provenance of organic matter in NW African dust over the Atlantic Ocean. Geochim. Geophys. Geosyst. 3, doi:10.1029/2001GC000269 (2002).
10. Gorricke, R., Montoya, J. P. & Try, B. In Stable Isotopes in Ecology and Environmental Science (eds Lajtha, K. & Menge, R. H.) 181–221 (Blackwell Scientific Publications, Oxford, UK, 1994).
11. Eglinston, T. J. et al Variability in radiocarbon ages of individual organic compounds from marine sediments. Science 277, 796–799 (1997).
12. Loh, A. N. Chemical, Isotopic and Microbical Characterization of Dissolved and Particulate Organic Matter in Eutrophic, Coastal and Open Ocean Systems. Doctoral dissertation, College of William and Mary (2002).
13. Wang, X.-C., Druffel, E. R. M., Griffin, S., Lee, C. & Kashgarian, M. Radiocarbon studies of organic compound classes in plankton and sediment of the northeastern Pacific Ocean. Geochim. Cosmochim. Acta 62, 1365–1378 (1998).
14. Hwang, J. & Druffel, E. R. M. Lipid-like material as the source of the uncharacterized organic carbon in the ocean. Science 299, 881–884 (2003).
15. Wang, S.-G., Hedges, J., Lee, C., Peterson, M. L. & Herline, P. J. Composition and transport of lipid biomarkers through the water column and surficial sediments of the equatorial Pacific Ocean. Deep-Sea Res. II 44, 2311–2316 (1997).
16. Aluwihare, L. I., Repeta, D. J. & Chen, R. F. Chemical composition and cycling of dissolved organic matter in the mid-Atlantic bight. Deep-Sea Res. II 49, 4421–4437 (2002).
17. Hedges, J. I. et al The molecularly-uncaracterized component of unilving organic matter in natural environments. Org. Geochem. 31, 945–958 (2000).
18. Aluwihare, L. I., Repeta, D. J. & Chen, R. F. The major biopolymeric component to dissolved organic carbon in surface seawater. Nature 387, 166–169 (1997).
19. Santschi, P. H. et al Isotopic evidence for the contemporary origin of high-molecular weight organic materials in oceanic environments. Geochim. Cosmochim. Acta 59, 625–631 (1995).
20. Druffel, E. R. M., Bauer, J. E., Griffin, S. & Hwang, S.-G. Formation of anthropogenic carbon into organic compounds in the deep ocean. Deep-Sea Res. Lett. 30, doi:10.1029/2002GL017423 (2003).
21. Clark, L. L., Ingall, E. D. & Benner, R. Marine phosphorus is selectively remineralised. Nature 393, 426 (1998).
22. Fuhrman, J. A. & Benfield, E. R. Black carbon in sea ice. Geophys. Res. Lett. 28, 3313–3319 (2001).
23. Hedges, J. I. & Keil, R. G. Sedimentary organic matter preservation: an assessment and speculative synthesis. Mar. Chem. 49, 81–115 (1995).
24. Trumbore, S. E. & Druffel, E. R. M. In The Role of Nonliving Organic Matter in the Earth’s Carbon Cycle (eds Zepf, R. G. & Sonnentag, C.) 7–22 (John Wiley & Sons, Chichester, UK, 1998).
25. Sotero, P. Preparation of carbon dioxide for stable carbon isotope analysis of petroleum fractions. Anal. Chem. 52, 1389–1391 (1980).
Impact of climate change on marine pelagic phenology and trophic mismatch

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Phenology, the study of annually recurring life cycle events such as the timing of migrations and flowering, can provide particularly sensitive indicators of climate change. Changes in phenology may be important to ecosystem function because the level of response to climate change may vary across functional groups and multiple trophic levels. The decoupling of phenological relationships will have important ramifications for trophic interactions, altering food-web structures and leading to eventual ecosystem-level changes. Temperate marine environments may be particularly vulnerable to these changes because the recruitment success of higher trophic levels is highly dependent on synchronization with pulsed planktonic production. Using long-term data of 66 plankton taxa during the period from 1958 to 2002, we investigated whether climate warming signals are emergent across all trophic levels and functional groups within an ecological community. Here we show that not only is the marine pelagic community responding to climate changes, but also that the level of response differs throughout the community and the seasonal cycle, leading to a mismatch between trophic levels and functional groups.

The vast majority of documented phenology studies relating seasonal shifts in biology to climate have come from terrestrial and limnological sources (see refs 5, 6). Furthermore, most studies have collectively remained relatively static, albeit with considerable (the central tendency; see Methods and Fig. 1a, b) were calculated using data from the Continuous Plankton Recorder (CPR), one of the longest and most spatially extensive marine biological data sets in the world.

The x axis of Fig. 1c shows the timing of the seasonal peaks in 1958 of all 66 plankton taxa used in the analysis; this represents the classical view of succession in the temperate marine pelagic ecosystem. Using the linear slope of the time series of the timing of the seasonal peak, we calculated the change in timing of the seasonal cycle (in months) from 1958 to 2002 for each taxon (Fig. 1c, y axis). Substantial temporal modifications in seasonal successional peaks have occurred over the past few decades. In particular, seasonal peaks of meroplankton have moved significantly (P < 0.0001) forward (for example, the phylum Echinodermata has moved by 47 days (d)). By contrast, diatom peaks in spring and autumn have collectively remained relatively static, albeit with considerable...

Figure 1 Changes in phenology throughout the pelagic season. a, Examples of seasonal cycles for two of the 66 taxa—the dinoflagellate Ceratium fusus and the diatom Cylindrotheca closterium—used in the analysis for the periods 1958–1980 and 1981–2002. The timing of the seasonal peaks, using the indicator of central tendency, is also shown. b, Inter-annual variability of the seasonal peak for the above two species from 1958 to 2002. c, The change in the timing of the seasonal peaks (in months) for the 66 taxa over the 45-yr period from 1958 to 2002 plotted against the timing of their seasonal peak in 1958. For each taxon, the linear regression in b was used to estimate the difference between the seasonal peak in 1958 and 2002. A negative difference between 1958 and 2002 indicates seasonal cycles are becoming earlier. Standard linear regression was considered appropriate because there was minimal autocorrelation (determined by the Durbin–Watson statistic) in the phenology time series.