Substantial loss of isoprene in the surface ocean due to chemical and biological consumption

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Isoprene contributes to the formation of ozone and secondary organic aerosol in the atmosphere, and thus influences cloud albedo and climate. Isoprene is ubiquitous in the surface open ocean where it is produced by phytoplankton, however emissions from the global ocean are poorly constrained, in part due to a lack of knowledge of oceanic sink or degradation terms. Here, we present analyses of ship-based seawater incubation experiments with samples from the Mediterranean, Atlantic, tropical Pacific and circum-Antarctic and Subantarctic oceans to determine chemical and biological isoprene consumption in the surface ocean. We find the total isoprene loss to be comprised of a constant chemical loss rate of $0.05 \pm 0.01 \text{ d}^{-1}$ and a biological consumption rate that varied between 0 and $0.59 \text{ d}^{-1}$ (median $0.03 \text{ d}^{-1}$) and was correlated with chlorophyll-a concentration. We suggest that isoprene consumption rates in the surface ocean are of similar magnitude or greater than ventilation rates to the atmosphere, especially in chlorophyll-a rich waters.
Isoprene (2-methyl-1,3-butadiene) emissions by terrestrial and marine life are altogether of a magnitude similar to the sum of natural and anthropogenic emissions of methane\(^1\)\(^{-2}\), ca. 500 TgC year\(^{-1}\). Owing to its reactivity and short lifetime in the atmosphere\(^3\) (minutes to hours), isoprene impacts atmospheric chemistry by forming tropospheric ozone, modifying the oxidation behaviour of other organic compounds, and contributing to secondary organic aerosols\(^4\)\(^{-5}\). Even though the oceans emit much less isoprene than vegetated land, the potential of biogenic isoprene sources over the vast oceans remote from anthropogenic sources\(^6\) is considered the result of microbial degradation and chemical oxidation\(^1\)\(^{-5}\), but it has never been measured. Likewise, the occurrence of isoprene-degrading bacteria in seawater has been demonstrated\(^20\)\(^{-21}\) and a significant microbial sink has been suggested\(^22\)\(^{-24}\), but it has not been experimentally confirmed, let alone measured, in natural conditions including natural concentrations.

We conducted seawater incubations with the aim to determine if isoprene was chemically and biologically consumed in the surface ocean. Detailed time courses with coastal seawater inferred on the kinetics of isoprene loss, and these kinetics were used to calculate loss rates from incubations conducted during four oceanographic expeditions across the Mediterranean Sea and the Atlantic Ocean, in the Tropical Pacific, and in Antarctic and Subantarctic waters. The obtained loss rate constants were compared with rate constants of air–sea flux and vertical mixing, and their variability across samples was examined by comparison with biological and environmental variables, with the aim to propose a predictive model that fills a major gap in the assessment of isoprene turnover in the surface ocean.

### Results and discussion

**Evidence for biological and chemical isoprene consumption in coastal seawater.** The time course of isoprene concentration in coastal seawater samples incubated in closed glass bottles at the in situ temperature and in the dark demonstrated sustained loss for at least 45 h (Fig. 1a). Enclosure without headspace prevented isoprene loss by ventilation, and darkness was assumed to arrest isoprene turnover in the surface ocean.

Estimations of the global ocean emission of isoprene have been attempted either by top-down (balancing modelled emissions to atmospheric observations) or bottom-up (modelling oceanic isoprene concentration and air–sea flux) approaches, and they diverge by one or two orders of magnitude\(^14\) (maximum range: 0.1–12 TgC year\(^{-1}\)). In general, top-down estimates are much higher, which implies that atmospheric measurements, as well as knowledge of the atmospheric processes, are insufficient to properly constrain the top-down models, and/or the bottom-up studies underestimate the net isoprene production. An extra isoprene source through photoproduction by surfactants in the sea surface microlayer was invoked and experimentally demonstrated\(^15\) but later esteemed not enough to resolve the large discrepancy\(^16\). In any case, the difficulties in constraining the global marine isoprene emission have evidenced that knowledge of the magnitude, drivers, distribution, and dynamics of isoprene cycling processes is still poor due to lack of measurements and depends too much on a number of assumptions and laboratory-based studies\(^11\)\(^{-14}\)\(^,\)^\(^17\).

It is thought that not all the isoprene produced by phytoplankton escapes to the atmosphere because part of it is degraded in seawater, but the actual proportion is unknown. Chemical oxidation is taken for granted\(^18\) because of isoprene’s high reactivity\(^19\), but it has never been measured. Likewise, the occurrence of isoprene-degrading bacteria in seawater has been demonstrated\(^20\)\(^{-21}\) and a significant microbial sink has been suggested\(^22\)\(^{-24}\), but it has not been experimentally confirmed, let alone measured, in natural conditions including natural concentrations.

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**Evidence for biological and chemical isoprene consumption in coastal seawater.** The time course of isoprene concentration in coastal seawater samples incubated in closed glass bottles at the in situ temperature and in the dark demonstrated sustained loss for at least 45 h (Fig. 1a). Enclosure without headspace prevented isoprene loss by ventilation, and darkness was assumed to arrest all or most of the biological production\(^25\) and any photochemical production\(^15\) or degradation. Thus, the measured loss was considered the result of microbial degradation and chemical oxidation. In most cases an exponential function fitted better the decay than a linear function (Supplementary Table 1), indicating first-order (concentration-dependent) kinetics for isoprene loss.

Incubation of microorganism-devoid (filtered through 0.2 µm) coastal seawater sampled next to seaweeds showed an isoprene loss (0.12 d\(^{-1}\)) that was half the loss in non-filtered water (0.20 d\(^{-1}\); Fig. 1b and Supplementary Table 2), implying that chemical oxidation accounted for half the total loss. Oxidation by OH\(^{•}\), the fastest amongst isoprene reactions with oxidative transients for which reaction rate data exist\(^19\), could account for the observed chemical loss. However, the possibility of oxidation by hitherto overlooked, pervasive oxidants like H\(_2\)O\(_2\) deserved consideration. The addition of unrealistically high concentrations of either H\(_2\)O\(_2\)
or the enzyme bromoperoxidase (BrPO), substantially speeded up the chemical loss (0.91 d\(^{-1}\) with 10 \(\mu\)mol H\(_2\)O\(_2\) L\(^{-1}\); 0.31 d\(^{-1}\) with 0.0025 units BrPO mL\(^{-1}\); Fig. 1b and Supplementary Table 2). Isoprene could have reacted with H\(_2\)O\(_2\) in seawater as it does in acidic aerosols\(^{26}\). Besides, should dissolved BrPOs from seaweeds or outer-membrane-bound\(^{28}\) BrPOs from phytoplankton occur, they would have reacted with added H\(_2\)O\(_2\) to produce hypobromous acid (HOBr), a strong oxidant\(^{29}\) that would further remove isoprene. Indeed, the addition of BrPO consumed isoprene because it produced HOBr by reaction with the naturally occurring H\(_2\)O\(_2\). Confirming this interpretation, large HOBr production by simultaneous addition of BrPO and H\(_2\)O\(_2\) caused complete isoprene removal in less than 4 h (Fig. 1b). Therefore, the results shown in Fig. 1b indicate that isoprene is reactive to pervasive H\(_2\)O\(_2\) either directly or through the formation of enzymatically derived HOBr. All in all, first-order total isoprene loss (Fig. 1a) is expected to depend on photochemically-produced oxidants\(^{30}\) like H\(_2\)O\(_2\), OH· and \(^1\)O\(_2\) as well as on microbiota through (a) microbial uptake and catabolism\(^{31}\) and (b) reaction with biologically produced oxidants\(^{26,31,32}\) like HOBr, H\(_2\)O\(_2\) or superoxide.

**Variability of isoprene loss rate constants in the open ocean.**

Ten of the eleven offshore experimental sites were located in the open ocean, and one was located on the Southwestern Atlantic Shelf. Altogether they covered wide ranges of latitude (40\(^\circ\)N–61\(^\circ\)S), sea surface temperature (–0.8–28.6 °C), daily-averaged wind speed (3–12 m s\(^{-1}\)), fluorometric chlorophyll-a (chl\(_a\)) concentration (0.1–5.8 mg m\(^{-3}\)), and isoprene concentration (4–104 nmol m\(^{-3}\)) (Fig. 2, Table 1 and Supplementary Table 3). Unfiltered seawater samples from the surface ocean were incubated in glass bottles for 24 h, at the in situ temperature and in the dark, and first-order loss rate constants were determined from initial and final isoprene concentrations (see Methods). Note that loss was determined under the assumption that isoprene production was arrested in the dark\(^{25}\). There is published evidence that residual isoprene production may occur in the dark\(^{33}\), but in our incubations, it was insufficient to counteract loss. Thus, isoprene losses caused by processes other than ventilation may have been underestimated.

Loss rate constants (\(k_{loss} = k_{bio} + k_{term}\)) varied over an order of magnitude, ranging 0.03–0.64 d\(^{-1}\) with a median of 0.08 d\(^{-1}\) (Table 1). They did not show any significant relationship to sea surface temperature (SST) (Supplementary Fig. 1) but showed proportionality to the chl\(_a\) concentration (Fig. 3a) that was best described by the following linear regression equation:

\[
k_{loss} = 0.10 \pm 0.01 \times [chl\(_a\)] + 0.05 \pm 0.01\]

The fact that the variability of \(k_{loss}\) is largely driven by [chl\(_a\)] suggests that the variable term (0.10 \(\times [chl\(_a\)]\)) corresponds to microbiota-dependent consumption (\(k_{bio}\)), which in our experiments gave values between 0 and 0.59 d\(^{-1}\), with a median of 0.03 d\(^{-1}\). These are the first experimental estimates of their kind and, hence, there are no other data to compare to. With a lack of experimental data, a pioneering modelling study\(^{18}\) proposed the use of a fixed \(k_{bio}\) at 0.06 d\(^{-1}\); more recently\(^{35}\), though, the need for a variable \(k_{bio}\) spanning at least between 0.01 and 0.1 d\(^{-1}\) was invoked to balance observed concentrations in situ with predictions of the production term from phytoplankton culture data once the ventilation and chemical losses were accounted for. Our experimental results indicate that such variable \(k_{bio}\) indeed exists and spans even a broader range. The most complete model of the global oceanic isoprene cycle to date\(^{17}\) also performed the best simulations with a variable \(k_{bio}\). This was computed proportional to the simulated [chl\(_a\)], with a proportionality coefficient of 0.054, i.e. roughly half the coefficient we obtained by linear regression of observations (0.10).

Part of the \(k_{loss}\) (or variable \(k_{loss}\)) is to be attributed to degradation or utilisation by heterotrophic bacteria. A pioneering study\(^{20}\) demonstrated the potential for bacterial consumption after isoprene additions at concentrations at least four orders of magnitude higher than natural concentrations. This has been accompanied by sparse but solid evidence\(^{20,21,34}\) for the presence in marine waters of isoprene-degrading bacteria belonging mainly to the phylum *Actinobacteria*. Two more recent studies\(^{24,35}\) suggested that members of the ubiquitous SAR11, the most abundant bacterial clade in the ocean, can also consume isoprene, but this was mainly based on indirect evidence and requires confirmation. Our \(k_{loss}\) did not show any significant correlation with the total bacterial abundance (Table 1). It must be noted, though, that bacterial abundance does not necessarily parallel heterotrophic bacterial activity, less so the activity of specific phyta, whereas a general trend of higher bacterial activity with higher [chl\(_a\)] is commonly observed\(^{36}\). Besides, phytoplankton-derived oxidants like the aforementioned H\(_2\)O\(_2\) and HOBr may have also contributed to the dependence of isoprene loss on [chl\(_a\)]. Circumstantial evidence in one study\(^{37}\) suggested that the cosmopolitan cyanobacterium *Synechococcus* might consume isoprene; it is worth noting that *Synechococcus* harbours membrane-bound BrPO\(^{38}\) and may, thus, consume isoprene as a side-process of combating oxidative stress caused by H\(_2\)O\(_2\). If confirmed, this could have contributed to the correlation between \(k_{loss}\) and [chl\(_a\)]. However, the three highest \(k_{loss}\) of our experimental series were measured in waters colder than 14 °C where *Synechococcus* occurred at very low biomass\(^{39,40}\). Therefore, these cyanobacteria cannot be invoked as responsible for the high \(k_{loss}\) paralleling high [chl\(_a\)], and a large proportion of the \(k_{bio}\) term of \(k_{loss}\) must correspond to degradation by heterotrophic bacteria\(^{34}\) as well as to reaction with biogenic oxidants from phytoplankton.

We attribute the intercept of Eq. (1) to a less variable loss by microbiota-independent chemical oxidation\(^{18}\), \(k_{chem}\). In remarkable support to this, the value of the intercept, 0.05 ± 0.01 d\(^{-1}\), coincides with the \(k_{chem}\) commonly prescribed in models hitherto\(^{17,18,41}\), which was calculated from reaction rate constants and estimated steady-state concentrations of photochemically-produced OH- and \(^1\)O\(_2\) in the surface ocean.

Despite the limited number of experiments, the fact that they cover a wide range of contrasting oceanic regions and conditions confers to Eq. (1) the potential to be used in numerical models of...
Table 1 Measured biological variables and isoprene process rate constants.

| sample (# on map)a | SST (°C) | Chla (mg m⁻³) | BA (10⁶ cell mL⁻¹) | isoprene (nmol m⁻³) | k_loss (d⁻¹) | k_vent (d⁻¹) | k_mix (d⁻¹) | total τ (d) | k_prod (d⁻¹) | sp. prod. rate (nmol (mg chla)⁻¹ d⁻¹) |
|---------------------|----------|----------------|-------------------|---------------------|--------------|-------------|------------|------------|-------------|-------------------------------------|
| Trop. Pacific 1     | 28.6     | 0.31           | 0.92              | 17.5                | 0.06         | 0.03        | −0.005b    | 11.2       | 0.08        | 4.8                                                 |
| Mediterranean 2      | 18.9     | 0.15           | 0.64              | 27.8                | 0.09         | 0.08        | −0.005b    | 6.0        | 0.16        | 29.9                                                |
|                     | 19.1     | 0.19           | 0.86              | 25.1                | 0.07         | 0.10        | −0.005b    | 6.0        | 0.16        | 21.3                                                |
|                     | 16.8     | 0.15           | 1.32              | 39.0                | 0.03         | 0.03        | −0.005b    | 15.5       | 0.06        | 15.8                                                |
| Atlantic 5           | 23.4     | 0.61           | 1.46              | 104.1               | 0.15         | 0.08        | −0.005b    | 4.4        | 0.22        | 37.9                                                |
|                     | 28.1     | 0.20           | 1.29              | 25.0                | 0.04         | 0.07        | −0.005b    | 9.3        | 0.10        | 13.0                                                |
|                     | 25.5     | 0.11           | 0.78              | 4.5                 | 0.08         | 0.11        | −0.005b    | 5.4        | 0.18        | 7.3                                                 |
|                     | 13.9     | 1.67           | 2.64              | 27.6                | 0.28         | 0.16        | −0.005b    | 2.3        | 0.44        | 7.2                                                 |
| S. Ocean 9           | 5.0      | 5.77           | 0.63              | 64.2                | 0.06         | 0.07        | 0.001      | 1.4        | 0.71        | 7.9                                                 |
|                     | 1.0      | 1.96           | 0.23              | 8.8                 | 0.19         | 0.06        | −0.005     | 4.0        | 0.25        | 1.1                                                 |
|                     | −0.8     | 0.29           | 0.36              | 6.3                 | 0.06         | 0.14        | −0.010     | 4.9        | 0.19        | 4.2                                                 |

STT sea surface temperature, chla chlorophyll-a concentration, BA bacterial abundance, k_loss rate constant of isoprene loss in incubations (microbial degradation + chemical oxidation), k_vent rate constant of isoprene ventilation to the atmosphere, k_mix rate constant of isoprene vertical mixing by turbulent diffusion at the bottom of the mixed layer (negative means import into the surface mixed layer), total τ turnover time due to all sinks, k_mix rate constant of isoprene production, assuming 24-h steady-state for the isoprene concentration, sp. prod. rate chlα-normalised daily rate of isoprene production.

aMap in Fig. 2; coordinates in Supplementary Table 2.

bTaken from the global integral suggested by a model17.

to compare among sensors, are validated against HPLC-measured chla42, not against the fluorometric chla that was used in Eq. (1).

To convert fluorometric to satellite chla concentrations we used a relationship obtained with a global compilation of in situ fluorometric measurements and their match-ups from SeaWiFS and MODIS Aqua sensors43:

\[
[chla_{sat}] = 0.79 \times [chla]^{0.78} (R^2 = 0.66, n > 1000) \tag{2}
\]

Substitution in Eq. (1) results in:

\[
k_{loss} = 0.14 \times [chla_{sat}]^{1.28} + 0.05 \tag{3}
\]

which is our recommended equation for k_loss prediction from satellite chla. Note that only the variable term (k_loss) changes from Eq. (1), while the intercept (k_chem) is maintained at 0.05 d⁻¹.

Comparison of isoprene sinks and total turnover time. The change of isoprene concentration ([iso]) in the surface mixed layer over time can be described as the budget of sources and sinks:

\[
\Delta[iso]/\Delta t = [iso] \cdot (k_{prod} - k_{loss} - k_{vent} - k_{mix}) \tag{4}
\]

where k_prod, k_vent, and k_mix are the rate constants of isoprene production, ventilation to the atmosphere, and vertical downward mixing by turbulent diffusion, respectively.

We calculated k_vent from our sampling sites over a period of 24 h (Table 1). Ventilation has been considered the main isoprene sink from the upper mixed layer of the ocean18. In our sampling sites, k_loss was 0.4 to 10 times the k_vent (median factor: 1.2). That is, loss through microbial + chemical consumption was of the same order as ventilation, sometimes considerably faster. Vertical mixing, k_mix, was estimated to be one order of magnitude lower than the other process rates (Table 1), and in all cases but one it was calculated or assumed not to be a loss term but an import term into the mixed layer, because vertical profiles generally show maximum isoprene concentrations below the mixed layer and turbulent diffusion causes upward transport14,17. Altogether, the microbial, chemical, ventilation, and, where relevant, mixing losses resulted in total turnover times (1/(k_loss + k_vent + k_mix)) of isoprene between 1.4 and 16 days, median 5 days (Table 1).
Isoprene production. Assuming steady-state for isoprene concentrations over 24 h (Supplementary Fig. 2), i.e. $\Delta [\text{iso}] / \Delta t = 0$ in Eq. (4), the sum of the daily rate constants of all sinks ($k_{\text{loss}} + k_{\text{vent}}$) equals the rate constant of isoprene production ($k_{\text{prod}}$), with $k_{\text{max}}$ adding to either side depending on whether it is an import to or an export from the mixed layer (Table 1). Note that $k_{\text{prod}}$ was the highest coinciding with higher [chl]a. This is consistent with a recent study\(^{14}\) where measurement of the net biological isoprene production (i.e. production — consumption rates) across seasons in the open ocean was attempted; net production rates increased in May, coinciding with a large increase in [chl]a and phytoplankton cell abundance.

The product of $k_{\text{prod}}$ by the isoprene concentration gives the daily isoprene production rate, which can be normalised by dividing it by the chl concentration. In our study, this specific isoprene production rate varied between 1 and 38 nmol (mg chl)\(^{-1}\) d\(^{-1}\) (Table 1), median 8 nmol (mg chl)\(^{-1}\) d\(^{-1}\). These values are within the broad range reported across phytoplankton taxa from laboratory studies with monocultures\(^{41-45}\) (0.3–32, median 3 nmol (mg chl)\(^{-1}\) d\(^{-1}\), $n = 124$). Five of the eleven sites gave values >13 nmol (mg chl)\(^{-1}\) d\(^{-1}\), i.e. in the higher end of the laboratory data range. This is not unexpected, since measurements in monoculture experiments are typically conducted before reaching nutrient limitation, below light saturation and in the absence of UV radiation, to mention three stressors commonly occurring in the surface open ocean. If isoprene biosynthesis and release is enhanced by any of these stressors, as is the case in vascular plants\(^{7,10}\), then monoculture-derived results will easily render underestimates of isoprene production in the open ocean. Production by heterotrophic bacteria\(^{46}\) could have also contributed to increase apparent isoprene production rates, but the occurrence and importance of this process in the marine environment is unknown.

When plotted against the SST, which was also the temperature of the incubations, specific isoprene production rates increased exponentially between −0.8 and 23 °C and dropped drastically at higher SST (Fig. 3b). Several studies with phytoplankton monocultures have reported positive dependence of specific isoprene production rates on temperature\(^{15,47–50}\). One of these studies\(^{45}\) described that the increase with temperature reaches an optimum for production that varies among phytoplankton strains and with light intensity, but falls around 23–26 °C. The most detailed study\(^{47}\) was conducted with a Prochlorococcus strain; remarkably, the shape of the specific production rate vs. temperature curve for this cyanobacterium strain was almost identical to that of Fig. 3b, with an exponential increase until 23 °C and a drop thereafter. This is the canonical curve type of enzymatic activities, but the thermal behaviour of the enzymes for isoprene synthesis in marine unicellular algae has not yet been characterised\(^{12}\).

Revising the magnitude and players of the marine isoprene cycle. Our results allow redrawing the isoprene cycle in the surface mixed layer of the ocean. Figure 4 sketches the magnitude of the rate constants for production and sinks presented in Table 1, averaged according to a chl concentration threshold: the blue and green arrows correspond to the experiments in waters with [chl]a lower and higher than 0.4 mg m\(^{-3}\), respectively. Isoprene production in productive (chl-richer) waters is faster than in oligotrophic (chl-poorer) waters. Vertical mixing is assumed to majorly constitute an input into the mixed layer, yet very small. Photochemical production and emission from surfactants\(^{15}\) in the surface microlayer of productive waters is depicted as uncertain. Among sinks, the microbiota-dependent consumption is much faster in productive waters; actually, the statistical uncertainty of Eq. (1) and the uneven distribution of incubation results along the [chl]a axis hamper resolving $k_{\text{bio}}$ in phytoplankton-poor waters (<0.4 mg m\(^{-3}\)), which represent nearly 80% of the area of the global surface ocean as a monthly average. Here, $k_{\text{loss}}$ can be anything between 0.03 and 0.09 d\(^{-1}\), and therefore $k_{\text{bio}}$ will be <0.04 d\(^{-1}\). Putative purely chemical oxidation is considered invariant irrespective of the chl content; consequently, the combined microbial + chemical loss is much faster in productive waters. The $k_{\text{vent}}$ for ventilation to the atmosphere is not significantly different between the two groups because it depends on wind speed and SST, which are both independent of [chl]a.

Note that this comparison applies to process rate constants $k$ (d\(^{-1}\)), which represent the velocities at which processes occur and are attributable to biological and environmental agents. The actual process rates (nmol m\(^{-3}\) d\(^{-1}\)) will result from multiplying each of these $k$ by the isoprene concentration, [iso]. Even though [iso] tends to increase with [chl]a, there is no such a thing as a globally valid proportionality between the two\(^{13,14,51}\) (Table 1). All in all, more
isoprene is produced in productive waters but more is consumed as well; therefore, predicting the resulting effect on isoprene concentrations and air–sea fluxes is not straightforward.

Concluding remarks. Until now, most of the focus of isoprene cycling studies had been on the production term, considering specific production rates by phytoplankton as though they were constitutive and shaped by phylogeny, with an occasional emphasis on how they are tuned by acclimation to environmental conditions. Even though teasing apart phylogeny and acclimation at the cross-basin and seasonal scales is not an easy task because species and community succession are interlinked with environmental stressors, our results call for a deeper exploration of the ecophysiological drivers of isoprene biosynthesis by phytoplankton. As a matter of fact, whilst isoprene production is grossly modulated by phytoplankton biomass and primary production (Fig. 4), the resulting isoprene concentration does not necessarily follow indicators of phytoplankton biomass such aschl but it is further influenced by environmental factors such as SST, chl, primary production (Fig. 4), and emission to the atmosphere can no longer be regarded as biologically derived oxidants. All in all, isoprene concentration is tightly coupled to production and can dominate over conditions even, vertical mixing, the resulting total turnover times of species under variable natural conditions if we are to reliably predict isoprene production in the ocean.

We also show that the loss terms in the cycle are more complex and variable than believed, with a microbiota-dependent sink that is tightly coupled to production and can dominate over ventilation in chl-rich waters (Fig. 4). Considering all sinks together (ventilation, biological and chemical loss and, on one occasion, vertical mixing), the resulting total turnover time of isoprene in the surface mixed layer of the open ocean are in the order of one or two weeks in oligotrophic waters but can be as short as 1 to 4 days in productive waters. The microorganisms and metabolic mechanisms involved in isoprene biological consumption warrant further investigation because this important sink will be regulated by triggers of microbial speciation and activity, potential co-metabolisms, and microbial mortality by predators and viruses. Our results also indicate that chemical consumption is more variable than estimated hitherto and has abiotic and biotic terms involving photochemically as well as biologically derived oxidants. All in all, isoprene concentration and emission to the atmosphere can no longer be regarded as controlled only by phytoplankton biomass and functional types, with fixed loss rates dominated by the physicochemical processes (air–sea exchange and oxidation), but rather intimately connected to the variable structure and dynamics of the pelagic microbial food web.

Methods

Sampling and physical measurements. Mediterranean coastal water samples were collected in March and May 2021 at the Blanes Bay Microbial Observatory site, over a 20 m water column, and in August 2021 at a rocky pier of the northern coast of the island of Móra, Spain (Supplementary Table 1); (b) isoprene production by phytoplankton, which is related to phytoplankton biomass and can dominate over conditions even, vertical mixing, the resulting total turnover times of species under variable natural conditions if we are to reliably predict isoprene production in the ocean.

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GC. Isoprene monitored as m/z 67 in selected ion monitoring mode, had a retention time of 2.4 min in the LTQ DR-VRX chromatographic column held at 35°C. The detection limit was 1 pmol L⁻¹, and the analytical precision was 5%. In HOTMIX, TransPEGASO and PEGASO, calibration was performed by injections of a gaseous mixture of isoprene in N₂. In BIOGAPS-Moorea and coastal water experiments, a liquid standard solution prepared in cold methanol and subsequently diluted in MilliQ water was used instead.

**Isoprene ventilation rate constant.** The isoprene ventilation or air–sea exchange fluxes (F_{vent}) in nmol m⁻² d⁻¹ were calculated as:

\[ F_{vent} = K_{vent} \times \Delta \text{[iso]} / \Delta \text{t} \]

where \([\text{iso}]\) is the isoprene concentration in surface seawater, \([\text{iso}]_s\) is the isoprene concentration in the air, \(K_{vent}\) is Henry's Law constant for isoprene, and \(\Delta \text{t}\) is the gas exchange velocity (cm h⁻¹). Air-side isoprene can be considered near zero and neglected for flux calculations because isoprene is highly reactive in the atmosphere, and it is largely supersaturated in the surface ocean. \(K_{vent}\) was estimated using:

\[ K_{vent} = 0.251 \times U_{10} \times \text{SST}/(665)^{0.5} \]

where \(U_{10}\) is the wind speed at 10 m (m s⁻¹), and Sc is the Schmidt number (non-dimensional). On cruises, the wind speed was measured by the ships' meteorological stations and averaged over a period of 24 h, which was the duration of the incubations. In offshore Moorea, we recorded wind speed on the boat with a portable Skywatch BLS200 micrometeorological station. This instantaneous wind speed was converted to the daily average by applying the factor between instantaneous and daily average wind speeds measured at the Gump Station offshore. Sc was computed as:

\[ Sc = 3913.15 + 162.13 \times \text{SST} + 2.67 \times \text{SST}^2 + 0.012 \times \text{SST}^3 \]

where SST is in degrees Celsius (°C). The error of the computed ventilation fluxes is estimated to be 20% to 25%. To convert the flux \(F_{vent}\) (nmol m⁻² d⁻¹) into the ventilation rate constant \(K_{vent}\) (d⁻¹), the flux was divided by the mixed layer depth (\(\text{ZML, m}\), m) and by the isoprene concentration (nmol m⁻³), assuming that the surface concentration was equal to the average concentration in the mixed layer. During HOTMIX and PEGASO, \(\text{ZML, m}\) was determined from CTD profiles as the depth at which density was 0.125 kg m⁻³ higher than that at 5 m. In the case of the TransPEGASO cruise and the BIOGAPS-Moorea expedition, where no CTD casts were conducted, we used the geo-localised monthly values of a global climatology.

**Isoprene vertical mixing rate constant.** In the case of the three PEGASO samples (sampling sites #9–11), \(K_{mix}\) was estimated from measured vertical profiles of isoprene concentration and the turbulent diffusion across the pycnocline (\(K_d\)). Thus, the vertical mixing flux at the bottom of the ML (\(F_{mix}\), nmol m⁻² d⁻¹) was calculated as:

\[ F_{mix} = K_{mix} \times \Delta [\text{iso}] \times \Delta z \]

where \(K_{mix} = 2.6 \text{ m}² \text{d}^{-1}\) (or 0.3 cm² s⁻¹) was the diffusion coefficient gradient across the pycnocline, and \(\Delta z\) (m) was the distance covered by this gradient. Depending on the location of the concentration maximum, \(F_{mix}\) was positive (loss term, export from the ML) or negative (gain term, import into the ML). \(K_{mix}\) was calculated by dividing \(F_{mix}\) by the surface isoprene concentration and \(\text{ZML, m}\) (determined from the CTD profiles as above). We note that using a wider range of \(K_{mix}\) for Southern Ocean location (31°S, 10.1–1.0 cm² s⁻¹) would give 0.3–3 times the estimates of \(K_{mix}\) at sampling sites 9–11; however, the contribution of \(K_{mix}\) to the calculation of \(K_{mix}\) is so small (compared to those of the other sinks) that the effect of the \(K_{mix}\) range on \(K_{mix}\) was only noticeable in #11 (5% of \(K_{mix}\)). For HOTMIX, TransPEGASO and BIOGAPS-Moorea, \(K_{mix}\) could not be estimated from in situ data and a fixed value of −0.005 d⁻¹ was taken from the global integral suggested by a model.

**Chlorophyll a concentration.** Seawater 250-ml samples were filtered on glass fibre filters, which were extracted with 90% acetone at 4°C in the dark for 24 h. The fluorescence of extracts was measured with a calibrated Turner Designs fluorometer.

**Bacterial abundance.** Aliquots of 2 ml of the initial sample were fixed with 1% paraformaldehyde plus 0.05% glutaraldehyde and stored frozen at −80°C. The numbers of heterotrophic bacteria were determined by flow cytometry (Cube 8, Partec) after staining with SYBR-Green63.

**Data availability**

All data needed to evaluate the conclusions are available in https://doi.org/10.5281/zenodo.5794234.

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Author contributions

RS designed the work, ran some of the experiments and measurements, processed data, made figures and wrote the paper with contributions from co-authors. PC-G ran most of the open-ocean experiments and isoprene measurements. PR-R processed data and made some of the figures. MM-N ran the consumption kinetics and oxidation experiments with coastal waters and one of the open-ocean experiments and processed data.

Competing interests

The authors declare no competing interests.

Additional information

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