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RESEARCH

Widespread Production of Polyunsaturated Aldehydes by Benthic Diatoms of the North Pacific Ocean's Salish Sea

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Abstract

Diatoms are key primary producers across marine, freshwater, and terrestrial ecosystems. They are responsible for photosynthesis and secondary production that, in part, support complex food webs. Diatoms can produce phytochemicals that have transtrophic ecological effects which increase their competitive fitness. Polyunsaturated aldehydes (PUAs) are one class of diatom-derived phytochemicals that are known to have allelopathic and anti-herbivory properties. The anti-herbivory capability of PUAs results from their negative effect on grazer fecundity. Since their discovery, research has focused on their production by pelagic marine diatoms, and their effects on copepod egg production, hatching success, and juvenile survival and development. Few investigations have explored PUA production by the prolific suite of benthic marine diatoms, despite their importance to coastal trophic systems. In this study, we tested eight species of benthic diatoms for the production of the bioactive PUAs 2,4-heptadienal, 2,4-octadienal, and 2,4-decadienal. Benthic diatom species were isolated from the Salish Sea, an inland sea within the North Pacific ecosystem. All species were found to be producers of at least two PUAs in detectable concentrations, with five species producing all three PUAs in quantifiable concentrations. Our results indicate that production of PUAs from Salish Sea benthic diatoms may be widespread, and thus these compounds may contribute to benthic coastal food web dynamics through heretofore unrecognized pathways. Future studies should expand the geographic scope of investigations into benthic diatom PUA production and explore the effects of benthic diatoms on benthic consumer fecundity.

Keywords Polyunsaturated aldehyde · Benthic diatom · Teratogenic · Phytochemical · Pacific Ocean · Survey

Introduction

Diatoms are microalgae that contribute approximately 40% to total marine, and 20% to total global primary production (Mann 1999; Falkowski et al. 2004; Harvey et al. 2019). Diatoms are known for their high production in nutrient-rich, coastal ecosystems (Armbrust 2009; Uitz et al. 2010), where seasonal blooms provide resources that support secondary production, robust fisheries, and diverse megafauna (Legendare 1990; Mann 1993). Their ability to fulfill such an instrumental role in marine ecosystems is, in part, a result of their high bottom-up (Thamatrakoln 2021) and top-down (Bjærke et al. 2015; Pančić et al. 2019) competitive fitness. Diatoms have fast intrinsic growth rates (Inomura et al. 2023), including under turbulent conditions (Köhler 1997), and high uptake rates (Rogato et al. 2015) and storage capabilities of nitrate (Stief et al. 2022). However, their strong competitive fitness also results from their production of bioactive phytotoxins with allelopathic and anti-predatory effects (e.g., Caldwell 2009).

One suite of diatom-derived phytochemicals with well-known transtrophic effects are the bioactive polyunsaturated aldehydes (PUAs). PUAs are a class of oxylipins produced by many pelagic (Wichard et al. 2005; Vidoudez

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et al. 2011a, 2011b), and some benthic diatom species (Jüttner et a. 2010; Pezzolesi et al. 2017; Ruocco et al. 2018). PUAs are synthesized through the enzyme-catalyzed oxidation of polyunsaturated fatty acids (e.g., eicosapentaenoic and hexadecatrienoic acid) that are released from diatom cells after cell damage (Orefice et al. 2022). PUAs are well-studied in the pelagic marine environment because they can reduce consumer fecundity, namely copepod zooplankton, through maternal effects (see review by Russo et al. 2019). While adults are not observably affected by PUAs, they have teratogenic effects on embryo and larval stages of diatom consumers, thus minimizing diatom grazing impact by way of reductions to female cohort sizes (i.e. future grazers). Previous research has found similar negative effects of dissolved PUAs on a wide range of organisms and life history stages using dissolved PUA molecules. Examples include reduced sperm motility in benthic invertebrates (Caldwell et al. 2004), delayed sea urchin embryo development (Romano et al. 2010; Ruocco et al. 2019), inhibition of oyster haemocyte cytoskeleton organization (Adolph et al. 2004), deformities in larval chordates (Lettieri et al. 2015), and antiproliferation and generation of programmed cell death in human cancer cell lines (Martinez Andrade et al. 2018).

Despite PUAs having negative effects on disparate taxa and life history stages of pelagic and benthic organisms, studies exploring the prevalence of PUA production by benthic diatoms are lacking. Extensive surveys of pelagic PUA-producing diatom species have been performed since their discovery (e.g., Wichard et al. 2005; Bartual et al. 2020). However, comparatively little work has examined PUA production by benthic diatom species. Scholz and Liebezeit (2019) surveyed mudflat benthic diatom production of PUA precursor molecules, polyunsaturated fatty acids, finding 19 of 25 species to be producers, but were unable to detect PUA molecules from single-species cultures. To our knowledge, only three studies have detected PUA production by marine benthic diatom isolates (five species total), with two being surveys conducted in European waters (Jüttner et al. 2010; Pezzolesi et al. 2017) and the other a result of a feeding experiment (Ruocco et al. 2018). In these surveys, while all isolated benthic diatoms produced PUAs of 5- to 11-carbon chains (C_5 to C_{11}), both noted that medium chain length PUAs like C_8 dominated the produced aldehyde pool.

In coastal regions, benthic diatoms play important roles in both benthic and pelagic food webs (e.g., Christianen et al. 2017) and carbon cycling (Serôdio and Lavaud 2020). Further, their consumers, organisms like mollusks and crustaceans, are economically important and help to sustain coastal economies (Cooley and Doney 2009). Given the importance of the marine benthic environment, knowing whether benthic diatoms are widespread producers of PUAs is necessary to gain a holistic understanding of the role benthic diatoms have in coastal food web ecology. In this study, we examined cell-wounded (particulate) PUA production from eight numerically dominant diatom species isolated from the North Pacific Salish Sea ecosystem. We focused on three commonly produced, bioactive PUAs (2,4-heptadienal, 2,4-octadienal, and 2,4-decadienal, hereafter referred to as heptadienal, octadienal, and decadienal, respectively). These PUAs are consistently detected in pelagic diatom PUA research (e.g.Wichard et al. 2005; Vidoudez et al. 2011a) and are shown to impact consumer fecundity or development (e.g., Caldwell et al. 2009; Ruocco et al. 2019). These results will inform our understanding of prevalence of PUA production by benthic diatoms and their potential to influence coastal food webs through teratogenic effects.

Methods

Reagents

All reagents were purchased from commercially available sources and used without further purification. Concentrations of standards used for instrument calibration accounted for the purity of individual standards.

Diatom Isolation and Cultivation

Salish Sea benthic diatom assemblages were collected from eelgrass blades during low tide events at Marine Park in Bellingham, Washington (48.7193° N, 122.5158° W) and from outdoor flow-through seawater tanks housed at the Shannon Point Marine Center in Anacortes, Washington (48.50805° N, 122.68427° W). Individual diatoms were isolated using a micropipettor and purified by washing several times using 9-well wash plates filled with autoclaved filtered seawater (AFSW). Once isolated, diatoms were placed into polycarbonate bottles with AFSW amended with F/4 growth medium. Cultures were routinely assessed for species purity but were not axenic of bacteria. Diatom species were visualized using a combination of dissecting, compound, and scanning electron microscopy (SEM), and species identified by cross-referencing with published sources.

Eight benthic diatom species were isolated and identified from the Salish Sea: *Fragilariopsis pseudonana*, *Licmophora communis*, *Licmophora flabellata*, *Cylindrotheca closterium*, *Fistulifera saprophila*, *Nitzschia* sp. a, *Nitzschia* sp. b, and *Navicula* sp. (Ehrenberg 1839; Hassle 1965; Lobban et al. 2011; Zgrundo et al. 2013; Kociolek et al. 1881; Fig. 1). A minor contamination in the *C. closterium* culture was found during SEM imaging, and the contaminant identified as *Navicula vara* (Andrzej and Ditmar 2000; Fig. 1e).

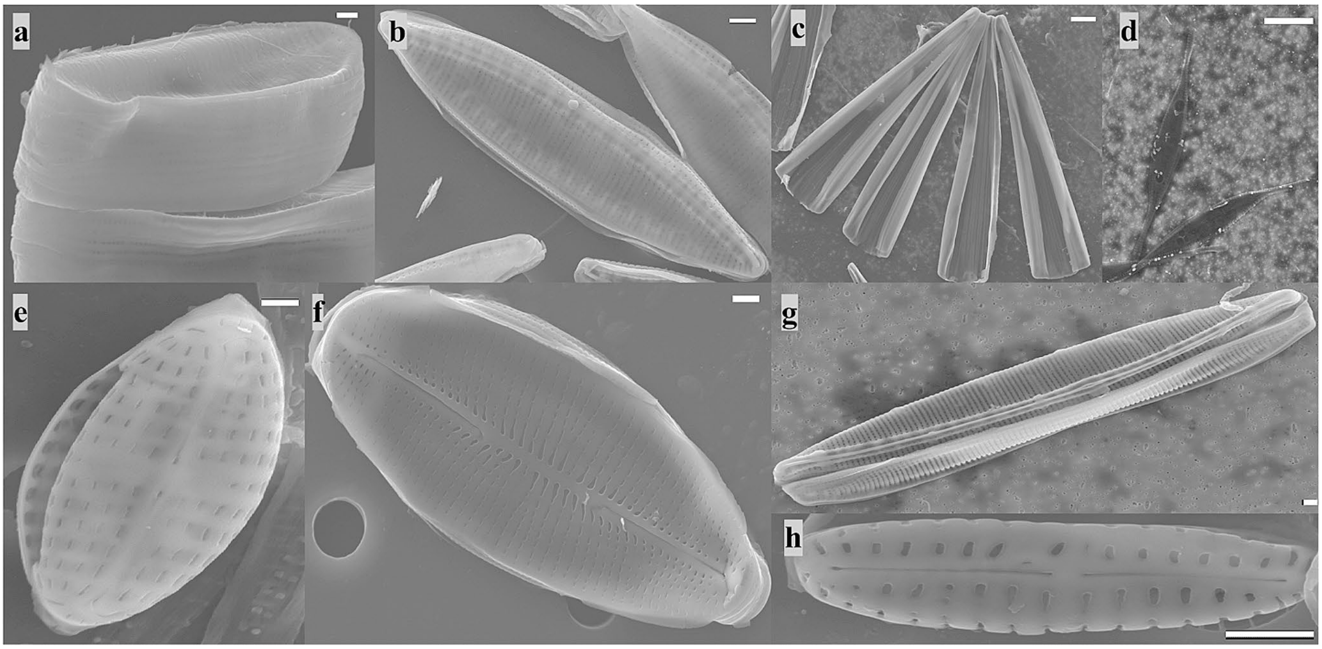

Fig. 1 Representative scanning electron micrographs used for identification of (**a**) *Fragilariopsis pseudonana*, (**b**) *Nitzschia* sp. a, (**c**) *Licmophora flabellata*, (**d**) *Cylindrotheca closterium*, (**e**) *Navicula vara*, (**f**) *Fistulifera saprophila*, (**g**) *Nitzschia* sp. b, and (**h**) *Navicula* sp. White scale bars depict 1 μm in all images but (**c**) and (**d**), which depict 10 μm

No SEM images were taken for *Licmophora communis*. Only *F. pseudonana* was deemed as a chaining diatom, while all others were single-celled pennate or community species.

Once isolated, diatom cultures were maintained in polycarbonate bottles (125 mL) using AFSW amended with F/4 growth medium. Cultures were grown in environmental incubators on a 11:13 light: dark cycle at 15 °C. Once per week, cultures were homogenized by gentle mixing, reduced by 75%, and refilled with growth medium.

Experimental Procedure

For PUA analysis, each benthic diatom species was dispersed into triplicate glass bowls covered with plastic wrap to minimize evaporation and filled with 200 mL AFSW amended with F/4 growth medium. After 6 days, each culture was homogenized, an aliquot (10 mL) removed for chlorophyll-*a* analysis, and the remaining volume (∽190 mL) processed for PUA analysis. Preliminary experiments with similar culture density and volumes indicated stationary phase for cultures - when PUA production is expected to be at its maximum (Ribalet et al. 2007) - was reached within 6 days of inoculation. Chlorophyll-*a* concentrations and PUA production data are presented as averages from analysis of these triplicate cultures.

Chlorophyll-*a* Quantification

Chlorophyll-*a* was used to standardize PUA production between the diatom cultures, as it is commonly used as a proxy for phytoplankton biomass (e.g., Jakobsen and Markager 2016) and is the primary pigment used by diatoms for photosynthesis (Kuczynska et al. 2015). Uniformly mixed culture aliquots (10 mL) were filtered onto GF/C (1.2 μm) glass fiber filters, placed in test tubes containing 90% acetone, and stored at -20 °C to allow for chlorophyll extraction. The next day, samples were brought to room temperature in darkness and decanted into glass test tubes. Chlorophyll-*a* was quantified using a Trilogy fluorometer on acidification mode by measuring fluorescence before and after acidification with 1 M hydrochloric acid (Lorenzen 1967).

PUA Extraction

Diatoms were vacuum filtered onto GF/C glass fiber filters. Vacuum was maintained under 500 mBar to prevent diatom cell wall disruption (Vidoudez et al. 2011a). Filters were transferred into glass vials containing *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA, 1 mL, 25 mM) in Tris/HCl (100 mM, pH 7.0) derivatization agent and benzaldehyde internal standard (5 μL, 1 mM) and frozen at -20 °C. Samples were thawed completely, and the freeze/thaw process was repeated twice more to ensure cell lysing. After the last thaw, samples were kept at room temperature for one hour to allow the derivatization reactions of released PUAs to occur. Samples were brought up in methanol, acidified with sulfuric acid (6 drops, 1 M), and extracted three times with hexane. Samples were centrifuged as needed to break any emulsion created by cell disruption. Hexane extracts were combined and water removed by addition of anhydrous sodium sulfate. Extracts were transferred to clean vials and brought to dryness under nitrogen. Residues were brought up in hexane (95 µL), transferred to a GC vial, and *n*-hexadecane-*d*34 (5 µL, 0.226 mg/mL) was added as a recovery standard. Samples were wrapped with Teflon tape and stored at -80 °C until gas chromatography with mass spectrometry detection (GC-MS) analysis the following day.

GC-MS Analysis

The instrument consisted of a HP 6890 gas chromatograph equipped with an Agilent 7683 autosampler coupled to a HP 5973 quadrupole mass spectrometer. Samples were injected in splitless mode and separated on a Agilent HP-5MS column (30 m, 0.250 mm internal diameter with 0.25 µm film thickness) programmed from 60 °C (2 min hold), ramped to 240 °C at 8 °C/min, then to 285 °C at 15 °C/min. Helium was used as the carrier gas at a constant flow of 1.5 mL/min. Data was collected in selective ion monitoring mode. PUA identification was performed using their molecular ions: *m/z* 305 (heptadienal), 319 (octadienal), and 347 (decadienal). Other monitored ions included: *m/z* 57 (alkanes), 66 (*n*-hexadecane-*d*34), 181 (all PFBHA-derivatized aldehydes), and 276 (all PUA molecules).

PUA Quantification

PUAs were quantified by comparing the benzaldehyde internal standard peak area to each PUA molecular ion. Recoveries were calculated based on peak areas of internal (benzaldehyde) and external (hexadecane-*d*34) standards, taking into account instrument response factors. Response factors were calculated via an external calibration curve. Method detection limit (MDL) and quantification limit (MQL) were determined following Glaser et al. (1981). These limits were used for quantifying PUAs produced by each culture. Quantifiable PUAs were standardized using measured chlorophyll-*a* values (nmol per µg chlorophyll-*a*). MDL and MQL values for analyzed PUA molecules are presented in Table 1.

Table 1 Method detection limits (MDL) and quantitation limits (MQL) for PUA molecules. Values were calculated using 6 replicate 0.001 nmol mixed PUA standards. MDL was calculated as 3σ and MQL as 10σ

Compound	MDL (nmol)	MQL (nmol)
2,4-heptadienal	0.00556	0.0185
2,4-octadienal	0.00526	0.0175
2,4-decadienal	0.00858	0.0286

Results

All eight benthic diatom species surveyed produced PUA molecules in detectable amounts (Fig. 2). The total concentration of PUAs produced varied between species, with the largest difference being 100 times more PUAs produced upon cell lysis in *F. pseudonana* than in *C. closterium*. The chain-forming species *F. pseudonana* produced the highest concentration of PUAs at 0.25 nmol/µg chlorophyll-*a*, almost three times more than the next highest concentration seen in *L. flabellata* at 0.085 nmol/µg chlorophyll-*a*. Across genus, *L. flabellata* produced almost ten times more PUA molecules than its counterpart *L. communis*, a difference not observed across *Nitzschia* species, where concentrations varied only 33% (Fig. 2).

Mean particulate PUA concentration also varied by PUA molecule, ranging from 0.6 pmol/µg chlorophyll-*a* (*L. communis*, decadienal) to 0.14 nmol/µg chlorophyll-*a* (*F. pseudonana*, octadienal). The largest inter-species PUA concentration range was seen in octadienal (Fig. 3). Both heptadienal and decadienal were produced by all eight diatom species, while octadienal was detected in seven of the eight species. Production of decadienal was two orders of magnitude lower than that of the other PUAs and was unquantifiable in some cultures. Interestingly, two diatom species that produced some of the highest concentrations of heptadienal and octadienal (*F. pseudonana* and *L. flabellata*) produced unquantifiable concentrations of decadienal. In addition, diatom species that produced quantifiable decadienal concentrations (excluding *F. saprophilia*) produced the lowest concentrations of both heptadienal and octadienal (Fig. 3).

Discussion

All eight benthic diatom species surveyed produced bioactive PUA molecules in detectable concentrations, with seven of the eight species producing all three of the monitored PUAs. Previously surveyed marine benthic diatom isolates commonly produced precursor polyunsaturated fatty acids but showed inconsistent production of PUAs (Pezzolesi et al. 2017; Scholz and Liebezeit 2012). PUA production surveys from pelagic diatom species showed similar variability in PUA production across species (e.g., Wichard et al. 2005), though the number of pelagic species surveyed is much higher than benthic species. Thus, it remains to be

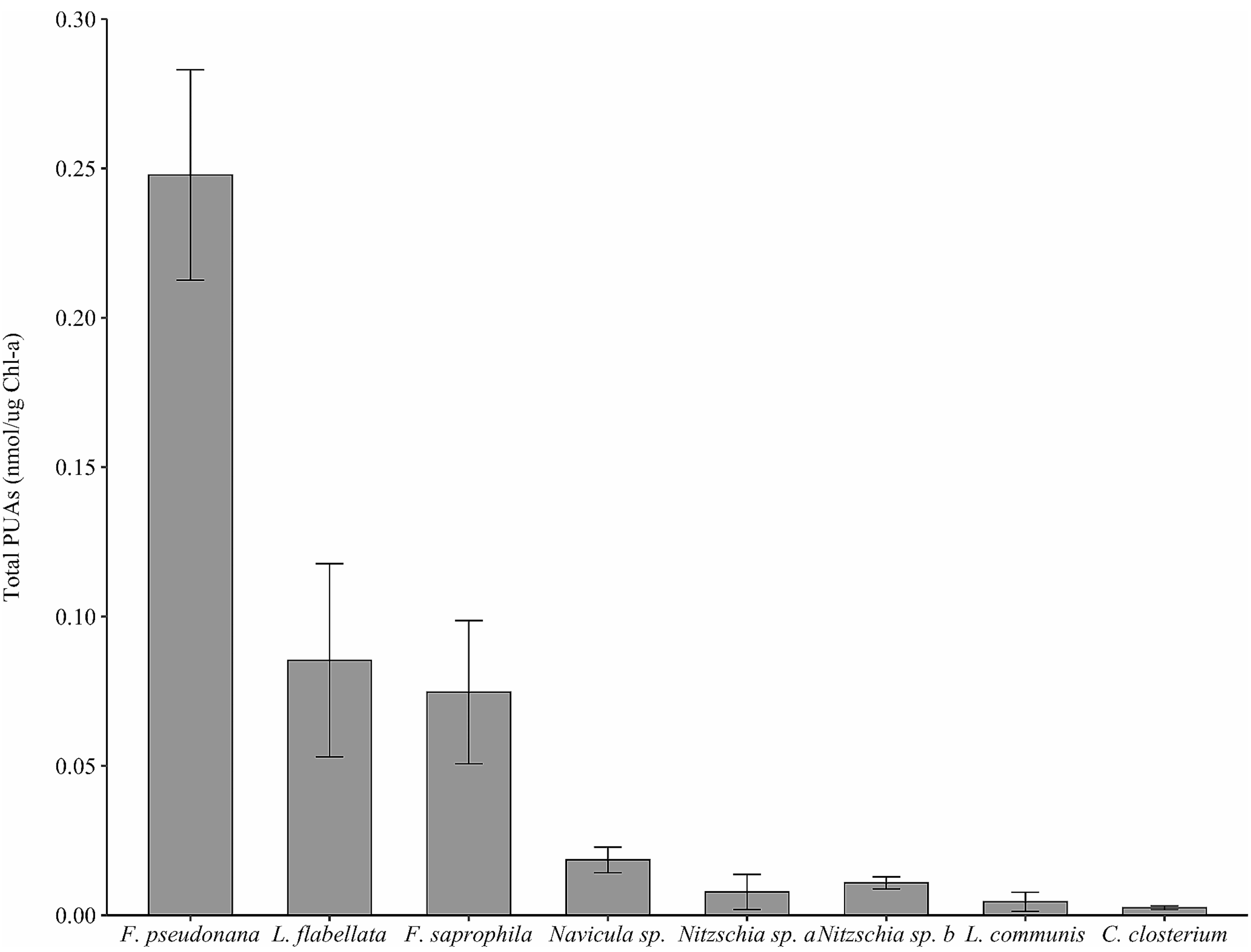

Fig. 2 Total PUA production of benthic diatoms. Gray bars represent means of quantifiable replicates and error bars represent standard deviations. Each diatom species tested was cultured in triplicate and quantified as nmol PUA molecule per µg of chlorophyll-*a*

determined how variable PUA production by benthic species is compared to their pelagic counterparts. In addition, one species surveyed, *C. closterium*, had previously been tested and deemed a non-producer of PUAs following a sea urchin fecundity experiment (Ruocco et al. 2018). However, our results indicate *C. closterium* is in fact a PUA producer, though it consistently produced the lowest quantifiable PUA concentrations of all diatoms tested (Fig. 3).

Across the individual PUA molecules, octadienal, an 8-carbon chain length PUA (C_8), was produced in the highest concentrations and decadienal (C_{10}) in the lowest. Pelagic PUA producer surveys have found heptadienal and other C_7 PUAs to be produced in the highest concentrations (Vidoudez et al. 2011a), contrasting with our results and other benthic surveys, where C_8 PUAs dominated (Jüttner et al. 2010; Pezzolesi et al. 2017). Across both pelagic and benthic surveys, decadienal and other C_{10} PUAs were consistently observed in lower concentrations over C_6, C_7, and C_8 PUAs, congruent with our findings (Wichard et al. 2005; Pezzolesi et al. 2017). This consistent result across all PUA producers indicates longer chain length PUAs like decadienal may be energetically unfavorable to form and are therefore produced in lower concentrations, with diatoms instead opting to produce shorter chain length molecules. Variation in PUA molecule production could also be related to the availability of precursor polyunsaturated fatty acids or lipoxygenase enzyme oxidation specificity (Orefice et al. 2022).

Some studies exploring the negative effects of PUAs on benthic invertebrate larvae have found a difference in bioactivity of PUA molecules, with decadienal having the highest bioactivity and octadienal the lowest (Varrella et al. 2014). A difference in PUA molecule bioactivity may explain why PUA molecules are produced in different concentrations within a population; higher bioactivity PUAs like decadienal are needed in lower concentrations to induce an effect (Romano et al. 2010), a finding consistent with the relative concentrations produced here. However, these

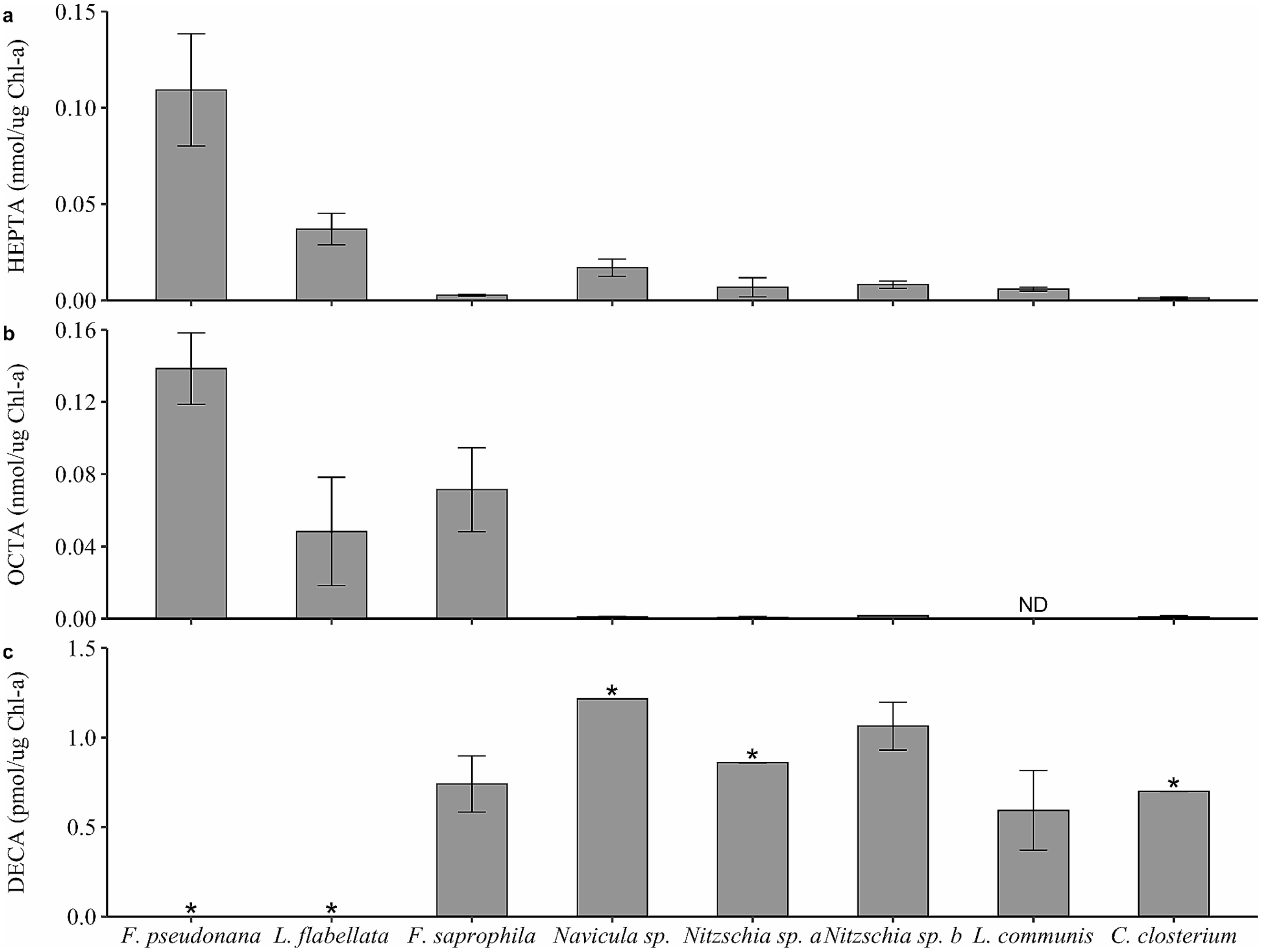

Fig. 3 Production of (**a**) 2,4-heptadienal (HEPTA), (**b**) 2,4-octadienal (OCTA), and (**c**) 2,4-decadienal (DECA) by benthic diatoms. Gray bars represent means of quantifiable replicates and error bars represent standard deviations. Each diatom species tested was cultured in triplicate and quantified as nmol or pmol PUA molecule per µg of chlorophyll-*a*. Species containing replicate cultures below method quantitation limit are marked with an asterisk. *L. communis* production of octadienal was below method detection limit and is marked with 'ND.' Note differences in scale and units of Y axes

PUA bioactivities were assessed using individual PUA molecules, whereas many species of diatoms produce mixtures of PUAs. Ruocco et al. (2019) showed that PUA mixtures have higher bioactivities in comparison to single PUAs, meaning diatom communities producing PUA mixtures can induce maternal effects at lower concentrations, increasing efficiency and thus their ecological fitness. This mixture synergy may evolutionarily explain why many diatoms can produce multiple PUA molecule types, a finding consistent with our results and other surveyed species (e.g., Wichard et al. 2005; Pezzolesi et al. 2017). However, the selectivity of diatoms opting to produce one PUA over another is yet to be explained.

Widespread production of PUAs in benthic diatoms of the Salish Sea has significant ecological implications. Studies of PUAs in the pelagic environment have shown negative impacts on consumer fecundity (e.g., Miralto et al. 1999; Ianora et al. 2004; Brugnano et al. 2016) and cause increased expression of stress-related genes in copepods in natural environments (Lauritano et al. 2016). Maternal copepod diets consisting of pelagic PUA-producing diatoms and gamete exposure to dissolved PUAs reduces egg viability, hatching success, and embryogenesis (Ban et al. 1997; Ianora et al. 1999; Lauritano et al. 2016). In the benthic environment, diatoms are the primary food source for many consumers, including protists (Haynert et al. 2020), mollusks (Kasim and Mukai 2006), and crustaceans (Zimba et al. 2016), which in turn support higher trophic level organisms. Studies have found similar teratogenic effects in the benthic environment when female sea urchins consumed common benthic diatom diets unknown to be PUA producers (Ruocco et al. 2018). In addition, benthic diatoms bloom in early spring, when benthic diatom-consuming invertebrates (e.g., intertidal snails) reproduce (Pardo and Johnson

2004). The synchrony of these events suggests that benthic diatoms could be a primary food source during invertebrate reproduction, meaning consumption of PUA-producing benthic diatoms could be a pathway for disrupted embryogenesis in invertebrate offspring. While no direct evidence of this has been observed in a natural environment, benthic diatom consumers link primary production to higher trophic levels of the pelagic and benthic environments (Christianen et al. 2017). Thus, benthic diatom production of PUAs could be impacting entire nearshore trophic systems.

The results of this study indicate that production of PUAs by benthic diatoms may be common. Future work should aim to survey more benthic diatom species for PUA production to further understand how ubiquitous production of PUAs is in the benthic environment. In addition, future studies should continue to explore the impact that PUA-producing benthic diatoms may have on the fecundity of their benthic consumers via predation. These could include organisms with diets dependent on benthic diatoms, or consumers that reproduce during seasonal benthic diatom blooms. These benthic consumer studies, along with continued benthic diatom PUA surveys, will allow for a greater understanding of the role benthic diatoms have in supporting secondary production in complex coastal food webs.

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Author Contributions J.J., M.B.O., and K.L. contributed to the study conception and design. J.J., M.B.O., K.L., and I.P. contributed to method development. Data collection was performed by J.J, I.P., and I.H., while data analysis was performed by J.J. The first draft of the manuscript was written by J.J., while comments and edits were made by M.B.O. and K.L. All authors read and approved the final manuscript.

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Data Availability Data is provided within the manuscript and raw data is available upon request.

Declarations

Competing Interests The authors declare no competing interests.

References

Adolph S, Bach S, Blondel M, Cueff A, Moreau M, Pohnert G, Poulet SA, Wichard T, Zuccaro A (2004) Cytotoxicity of diatom-derived oxylipins in organisms belonging to different phyla. J Exp Biol 207(17):2935–2946. https://doi.org/10.1242/jeb.01105

Andrzej W, Ditmar LB (2000) Diatom flora of marine coasts I. Iconographia Diatomologica 7:925

Armbrust EV (2009) The life of diatoms in the world's oceans. Nature 459(7244):185–192. https://doi.org/10.1038/nature08057

Ban S, Burns C, Castel J, Chaudron Y, Christou E, Escribano R, Umani SF, Gasparini S, Ruiz FG, Hoffmeyer M, Ianora A, Kang H-K, Laabir M, Lacoste A, Miralto A, Ning X, Poulet S, Rodriguez V, Runge J, Shi J, Starr M, Uye S, Wang Y (1997) The paradox of diatom-copepod interactions. Mar Ecol Prog Ser 157:287–293

Bartual A, Hernanz-Torrijos M, Sala I, Ortega MJ, González-García C, Bolado-Penagos M, López-Urrutia A, Romero-Martínez L, Lubián LM, Bruno M et al (2020) Types and distribution of bioactive polyunsaturated aldehydes in a gradient from mesotrophic to oligotrophic waters in the Alborán Sea (Western Mediterranean). Mar Drugs 18(3):159. https://doi.org/10.3390/md18030159

Bjærke O, Jonsson PR, Alam A, Selander E (2015) Is chain length in phytoplankton regulated to evade predation? J Plankton Res 37(6):1110–1119. https://doi.org/10.1093/plankt/fbv076

Brugnano C, Granata A, Guglielmo L, Minutoli R, Zagami G, Ianora A (2016) The deleterious effect of diatoms on the biomass and growth o early stages of their copepod grazers. J Exp Mar Biol Ecol 476:41–49. https://doi.org/10.1016/j.jembe.2015.11.015

Caldwell GS (2009) The influence of bioactive oxylipins from marine diatoms on invertebrate reproduction and development. Mar Drugs 7(3):367–400. https://doi.org/10.3390/md7030367

Caldwell GS, Bentley MG, Olive PJW (2004) First evidence of sperm motility inhibition by the diatom aldehyde 2E,4E-decadienal. Mar Ecol Prog Ser 273:97–108. https://doi.org/10.3354/meps273097

Christianen MJA, Middelburg JJ, Holthuijsen SJ, Jouta J, Compton TJ, van der Heide T, Piersma T, Sinninghe Damsté JS, van der Veer HW, Schouten S, Olff H (2017) Benthic primary producers are key to sustain the Wadden Sea food web: stable carbon isotope analysis at landscape scale. Ecology 98(6):1498–1512. https://doi.org/10.1002/ecy.1837

Cooley SR, Doney SC (2009) Anticipating ocean acidification's economic consequences for commercial fisheries. Environ Res Lett 4(2):024007. https://doi.org/10.1088/1748-9326/4/2/024007

Ehrenberg CG (1839) Über jetzt wirklich noch zahlreich lebende thierarten der Kreideformation der erde. 152–159

Falkowski PG, Katz ME, Knoll AH, Quigg A, Raven JA, Schofield O, Taylor FJR (2004) The evolution of modern eukaryotic phytoplankton. Science 305(5682):354–360. https://doi.org/10.1126/science.1095964

Glaser J, Foerst D, McKee G, Quave S, Budde W (1981) Trace analyses for wastewaters. Environ Sci Technol 15(12):1426–1435. https://doi.org/10.1021/es00094a002

Harvey BP, Agostini S, Kon K, Wada S, Hall-Spencer JM (2019) Diatoms dominate and alter marine food-webs when CO_2 rises. Diversity 11(12):242. https://doi.org/10.3390/d11120242

Hasle GR (1965) *Nitzschia* and *Fragilariopsis* species studied in the light and electron microscope III. The genus *Fragilariopsis*. Norske Videnskaps-Akademi *21*, 21–22

Haynert K, Gluderer F, Pollierer MM, Scheu S, Wehrmann A (2020) Food spectrum and habitat-specific diets of benthic foraminifera from the Wadden Sea – a fatty acid biomarker approach. Front Mar Sci *7*

Ianora A, Miralto A, Poulet SA (1999) Are diatoms good or toxic for copepods? Reply to comment by Jónasdóttir et al. Mar Ecol Prog Ser 177:305–308

Ianora A, Miralto A, Poulet SA, Carotenuto Y, Buttino I, Romano G, Casotti R, Pohnert G, Wichard T, Colucci-D'Amato L, Terrazzano G, Smetacek V (2004) Aldehyde suppression of copepod recruitment in blooms of a ubiquitous planktonic diatom. Nature 429(6990):403–407. https://doi.org/10.1038/nature02526

Inomura K, Pierella Karlusich JJ, Dutkiewicz S, Deutsch C, Harrison PJ, Bowler C (2023) High growth rate of diatoms explained by reduced carbon requirement and low energy cost of silica deposition. Microbiol Spectr 11(3):e03311–e03322. https://doi.org/10.1128/spectrum.03311-22

Jakobsen HH, Markager S (2016) Carbon-to-chlorophyll ratio for phytoplankton in temperate coastal waters: seasonal patterns and relationship to nutrients. Limnol Oceanogr 61(5):1853–1868

Jüttner F, Messina P, Patalano C, Zupo V (2010) Odour compounds of the diatom *Cocconeis scutellum*: effects on benthic herbivores living on *Posidonia oceanica*. Mar Ecol Prog Ser 400:63–73. https://doi.org/10.3354/meps08381

Kasim M, Mukai H (2006) Contribution of benthic and epiphytic diatoms to clam and oyster production in the akkeshi-ko estuary. J Oceanogr 62:267–281. https://doi.org/10.1007/s10872-006-0051-9

Kociolek JP, Blanco S, Coste M, Ector L, Liu Y, Karthick B, Kulikovskiy M, Lundholm N, Ludwig T, Potapova M, Rimet F, Sabbe K, Sala S, Sar E, Taylor J, Van de Vijver B, Wetzel CE, Williams DM, Witkowski A, Witkowski (1881) J *Licmophora communis* DiatomBase

Köhler J (1997) Measurement of *in situ* growth rates of phytoplankton under conditions of simulated turbulence. J Plankton Res 19(7):849–862. https://doi.org/10.1093/plankt/19.7.849

Kuczynska P, Jemiola-Rzeminska M, Strzalka K (2015) Photosynthetic pigments in diatoms. Mar Drugs 13(9):5847–5881. https://doi.org/10.3390/md13095847

Lauritano C, Romano G, Roncalli V, Amoresano A, Fontanarosa C, Bastianini M, Braga F, Carotenuto Y, Ianora A (2016) New Oxylipins produced at the end of a diatom bloom and their effects on copepod reproductive success and gene expression levels. Harmful Algae 55:221–229. https://doi.org/10.1016/j.hal.2016.03.015

Legendre L (1990) The significance of microalgal blooms for fisheries and for the export of particulate organic carbon in oceans. J Plankton Res 12(4):681–699. https://doi.org/10.1093/plankt/12.4.681

Lettieri A, Esposito R, Ianora A, Spagnuolo A (2015) *Ciona intestinalis* as a marine model system to study some key developmental genes targeted by the diatom-derived aldehyde decadienal. Mar Drugs 13(3):1451–1465. https://doi.org/10.3390/md13031451

Lobban C, Schefter M, Ruck E (2011) Licmophora flucticulata sp. nov. (Licmophoraceae, Bacillariophyceae), an unusual flabellate species from Guam and Palau. Phycologia 50:11–22. https://doi.org/10.2216/09-85.1

Lorenzen CJ (1967) Determination of chlorophyll and pheo-pigments: spectrophotometric equations. Limnol Oceanogr 12(2):343–346. https://doi.org/10.4319/lo.1967.12.2.0343

Mann DG (1993) Patterns of sexual reproduction in diatoms. Hydrobiologia 269(1):11–20. https://doi.org/10.1007/BF00027999

Mann DG (1999) The species concept in diatoms. Phycologia 38(6):437–495. https://doi.org/10.2216/i0031-8884-38-6-437.1

Martínez Andrade KA, Lauritano C, Romano G, Ianora A (2018) Marine microalgae with anti-cancer properties. Mar Drugs 16(5):165. https://doi.org/10.3390/md16050165

Miralto A, Barone G, Romano G, Poulet SA, Ianora A, Russo GL, Buttino I, Mazzarella G, Laabir M, Cabrini M, Giacobbe MG (1999) The insidious effect of diatoms on copepod reproduction. Nature 402(6758):173–176. https://doi.org/10.1038/46023

Orefice I, Di Dato V, Sardo A, Lauritano C, Romano G (2022) Lipid mediators in marine diatoms. Aquat Ecol 56(2):377–397. https://doi.org/10.1007/s10452-021-09932-8

Pančić M, Torres RR, Almeda R, Kiørboe T (2019) Silicified cell walls as a defensive trait in diatoms. *Proceedings of the Royal Society 286*https://doi.org/10.1098/rspb.2019.0184

Pardo LM, Johnson LE (2004) Activity and shelter use of an intertidal snail: effects of sex, reproductive condition and tidal cycle. J Exp Mar Biol Ecol 301(2):175–191. https://doi.org/10.1016/j.jembe.2003.09.017

Pezzolesi L, Pichierri S, Samorì C, Totti C, Pistocchi R (2017) PUFAs and PUAs production in three benthic diatoms from the northern Adriatic Sea. Phytochemistry 142:85–91. https://doi.org/10.1016/j.phytochem.2017.06.018

Ribalet F, Wichard T, Pohnert G, Ianora A, Miralto A, Casotti R (2007) Age and nutrient limitation enhance polyunsaturated aldehyde production in marine diatoms. Phytochemistry 68(15):2059–2067. https://doi.org/10.1016/j.phytochem.2007.05.012

Rogato A, Amato A, Iudicone D, Chiurazzi M, Ferrante MI, d'Alcalà MR (2015) The diatom molecular toolkit to handle nitrogen uptake. Mar Genom 24:95–108. https://doi.org/10.1016/j.margen.2015.05.018

Romano G, Miralto A, Ianora A (2010) Teratogenic effects of diatom metabolites on sea urchin *Paracentrotus lividus* embryos. Mar Drugs 8(4):950–967. https://doi.org/10.3390/md8040950

Ruocco N, Costantini S, Zupo V, Lauritano C, Caramiello D, Ianora A, Budillon A, Romano G, Nuzzo G, D'Ippolito G, Fontana A, Costantini M (2018) Toxigenic effects of two benthic diatoms upon grazing activity of the sea urchin: morphological, metabolomic and de novo transcriptomic analysis. Sci Rep 8(1):5622. https://doi.org/10.1038/s41598-018-24023-9

Ruocco N, Annunziata C, Ianora A, Libralato G, Manfra L, Costantini S, Costantini M (2019) Toxicity of diatom-derived polyunsaturated aldehyde mixtures on sea urchin *Paracentrotus lividus* development. Sci Rep 9(1):517. https://doi.org/10.1038/s41598-018-37546-y

Russo E, Ianora A, Carotenuto Y (2019) Re-shaping marine plankton communities: effects of diatom oxylipins on copepods and beyond. Mar Biol 166:9. https://doi.org/10.1007/s00227-018-3456-2

Scholz B, Liebezeit G (2012) Screening for competition effects and allelochemicals in benthic marine diatoms and cyanobacteria isolated from an intertidal flat (southern North Sea). Phycologia 51. https://doi.org/10.2216/11-80.1

Serôdio J, Lavaud J (2020) Diatoms and their ecological importance. In: Leal Filho W, Azul AM, Brandli L, Lange Salvia A, Wall T (eds) Life below Water. Encyclopedia of the UN Sustainable Development Goals. Springer, Cham. https://doi.org/10.1007/978-3-319-71064-8_12-1

Stief P, Schauberger C, Lund MB et al (2022) Intracellular nitrate storage by diatoms can be an important nitrogen pool in freshwater and marine ecosystems. Commun Earth Environ 3:154. https://doi.org/10.1038/s43247-022-00485-8

Thamatrakoln K (2021) Diatom ecophysiology: crossing signals on the road to recovery from nutrient deprivation. Curr Biol 31(5):253–254. https://doi.org/10.1016/j.cub.2021.01.016

Uitz J, Claustre H, Gentili B, Stramski D (2010) Phytoplankton class-specific primary production in the world's oceans: Seasonal and interannual variability from satellite observations. Glob Biogeochem Cycles 24:3016. https://doi.org/10.1029/2009GB003680

Varrella S, Romano G, Ianora A, Bentley MG, Ruocco N, Costantini M (2014) Molecular response to toxic diatom-derived aldehydes in the sea urchin Paracentrotus lividus. Mar Drugs 12(4):2089–2113. https://doi.org/10.3390/md12042089

Vidoudez C, Nejstgaard JC, Jakobsen HH, Pohnert G (2011) Dynamics of dissolved and particulate polyunsaturated aldehydes in mesocosms inoculated with different densities of the diatom *Skeletonema Marinoi*. Mar Drugs 9(3):345–358. https://doi.org/10.3390/md9030345

Vidoudez C, Casotti R, Bastianini M, Pohnert G (2011a) Quantification of dissolved and particulate polyunsaturated aldehydes in the Adriatic Sea. Mar Drugs 9(4):500–513. https://doi.org/10.3390/md9040500

Wichard T, Poulet SA, Halsband-Lenk C, Albaina A, Harris R, Liu DY, Pohnert G (2005) Survey of the chemical defence potential of diatoms: screening of fifty one species for alpha,beta,gamma,delta-unsaturated aldehydes. J Chem Ecol 31(4):949–958. https://doi.org/10.1007/s10886-005-3615-z

Zgrundo A, Lemke P, Pniewski F, Cox EJ, Lata A (2013) Morphological and molecular phylogenetic studies on *Fistulifera saprophila*. Diatom Res 28(4):431–443

Zimba PV, Hill EM, Withers K (2016) Benthic microalgae serve as the major food resource for porcelain crabs (*Petrolisthes* spp.) in oyster reefs: gut content and pigment evidence. J Exp Mar Biol Ecol 483:53–58. https://doi.org/10.1016/j.jembe.2016.06.005

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