LETTERS
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Rapid downward transport of the neurotoxin domoic acid in coastal waters

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Toxic phytoplankton blooms threaten coastlines worldwide by diminishing beach quality and adversely affecting marine ecosystems and human health[1,2]. The common diatom genus *Pseudo-nitzschia* consists of several species known to produce the neurotoxin domoic acid[3]. Recent studies suggest that algal blooms dominated by *Pseudo-nitzschia* are increasing in frequency and duration owing to changes in coastal nutrient regimes[1,4,5]. However, few studies have examined the persistence or long-term biogeochemical cycling of domoic acid in marine waters[6–8]. Here, we measure the concentration of domoic acid in surface waters and sediment traps—up to 800 m in depth—off the coast of Southern California. We show that peaks in *Pseudo-nitzschia* abundance and domoic acid concentrations in surface waters coincide with peaks in diatom and toxin abundance at depth, suggesting rapid downward transport of the toxin. In some cases, the sinking particles contain over five times the United States federal limit of domoic acid. Detection of domoic acid in bottom sediments indicates that the toxin may persist long after the *Pseudo-nitzschia* blooms. Our results indicate that vertical fluxes of domoic acid are a substantial source of the toxin to deep-ocean food webs, and could explain high levels of domoic acid previously observed in benthic organisms[9,10].

Pseudo-nitzschia species have been implicated in toxic blooms throughout coastal waters of Europe (for example Scotland, Spain), Asia (South Korea) and along the coasts of North America[3]. In western US waters, where *Pseudo-nitzschia* blooms seasonally, toxic cells are commonly consumed by sardines and anchovies, and the corresponding trophic transfer to higher organisms has resulted in mortalities of cetaceans, California sea lions and marine birds[11–13]. Consumption of seafood contaminated domoic acid (DA) can also affect humans, causing symptoms from mild gastrointestinal illness and headaches to memory loss, disorientation, seizures and even death[14]. Preventative beach closures help avert human illness, but closures are becoming increasingly routine and result in millions of dollars in economic losses[2].

The factors that govern the inception and demise of *Pseudo-nitzschia* blooms are poorly understood, particularly with respect to DA fate and persistence in coastal waters. Most field studies have focused on documenting toxin concentrations and *Pseudo-nitzschia* cell abundances in the upper water column (<100 m water depth)[3]. With the exception of one study[15], which presented DA concentrations in three sediment-trap samples, previous sediment-trap surveys examined *Pseudo-nitzschia* presence but not cell toxicity at greater depth[4,16]. The high solubility of DA in sea water[17] should result in the loss of toxin from *Pseudo-nitzschia* cells as they sink to depth, reducing the impact on benthic ecosystems. Nonetheless, sizeable concentrations of DA, reaching 700 μg DA per g tissue, have been documented in nearshore and intertidal filter and deposit feeding benthic communities[18,19] and in offshore organisms that feed on the benthos[9,20]. Until now, the mechanisms of DA transfer have remained unresolved. Here, we present the first study to examine particulate DA fluxes at depth using sediment traps deployed in two basins along the coast of Southern California. Coupled with surface-water measurements, we illustrate that vertical transport of DA occurs in rapid pulses that are closely tied to the timing of episodic surface blooms, with concentrations at depths greater than 800 m exceeding 100,000 ng DA per g dry sed. wt.

Deep-moored sediment traps were deployed in the Santa Barbara Basin (SBB) (November 2004–June 2006) and the San Pedro Basin (SPB) (April 2006–December 2007) (Fig. 1). The SBB mooring was located near the basin centre with the trap positioned at a depth of 540 m (~50 m above the bottom). Two additional traps were placed at depths of 550 and 800 m on the SPB mooring in a total water depth of ~900 m. Sinking particles were collected during consecutive two-week and one-week intervals in the SBB and SPB traps, respectively. Trap-cup solutions were preserved with 10% sodium azide (SBB) and 2% formaldehyde (SPB) to prevent degradation of organic material and to retard grazing by swimmers. In SBB, DA was measured both in sediment-trap particulates and in the trap solution. This approach accounts for possible leaching of the toxin from the particulate phase to the dissolved phase during sediment-trap deployment. For SPB samples, a wet split of the trap material was used for analysis, therefore combining particulate and dissolved

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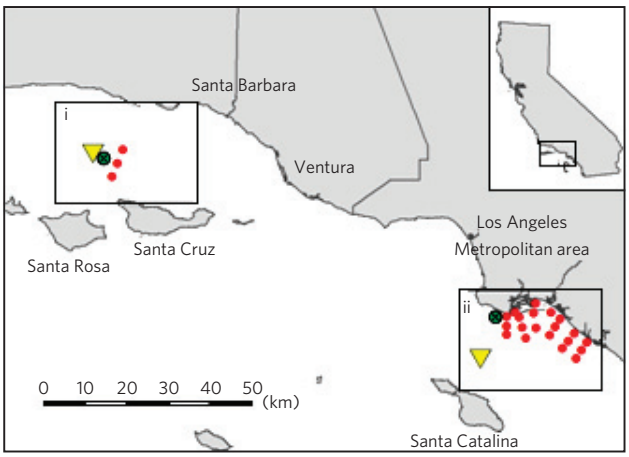

Figure 1 | Santa Barbara Basin (SBB) and San Pedro Basin (SPB) sampling sites. Locations of sediment traps (yellow inverted triangles), surface water sampling sites (red circles) and sediment cores (green circles) in SBB (i) and SPB (ii). Data from surface water sites (red circles) were averaged for comparison with the sediment trap(s) in each basin.

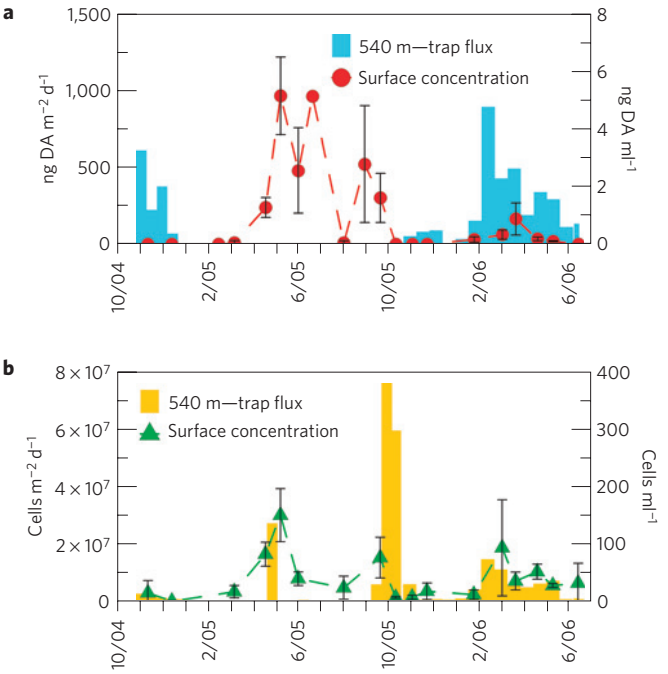

Figure 2 | Domoic acid and *Pseudo-nitzschia* cell measurements in sediment-trap material and surface waters of Santa Barbara Basin. **a**,**b**, Comparisons of sediment-trap (540 m) and surface DA (**a**) and *Pseudo-nitzschia* (**b**) measurements from November 2004 to July 2006. The trap values are expressed in terms of flux whereas surface quantities are in concentration. The bar width reflects the duration of trap-cup collection. Surface values are an average of three sampling sites near the trap location, with error bars reflecting one standard deviation. Missing trap data points are due to trap clogs or unavailability of trap material.

contributions in one measurement. DA was analysed using liquid chromatography–mass spectroscopy (LC-MS/MS; ref. 21) and an enzyme-linked immunosorbent assay (ELISA; ref. 15) in the SBB and SPB, respectively. DA concentrations and *Pseudo-nitzschia* abundance measurements at three surface stations (0–1 m) in close proximity to the SBB sediment trap were averaged from monthly measurements and used to correlate sediment-trap results with surface blooms[22] (Fig. 1(i)). For the SPB, surface (0–1 m) DA measurements were averaged from 20 stations sampled on a weekly to monthly basis[15] (Fig. 1(ii)).

Elevated *Pseudo-nitzschia* abundance and DA concentrations in surface waters were largely coincident, with high *Pseudo-nitzschia* and DA fluxes observed at depth in SBB and SPB (Figs 2, 3). DA concentrations varied from less than 34 to 420 ng DA per g dry sed. wt in the SBB trap (540 m). In the SPB, DA concentrations reached 49,900 ng DA per g dry sed. wt in the 550 m trap and 163,000 ng DA per g dry sed. wt in the 800 m trap. These concentrations are as much as eight times the US federal regulatory limit for DA in shellfish (20,000 ng DA per g tissue; ref. 3) and suggests the heightened potential for bioaccumulation by mesopelagic and benthic feeders. In both basins a wide range in DA fluxes was observed, with SBB DA fluxes (540 m) ranging from less than 20 to 890 ng DA m^{-2} d^{-1} (Fig. 2a), whereas in SPB DA fluxes reached upwards of 24,200 ng DA m^{-2} d^{-1} in the 550 m trap and 19,800 ng DA m^{-2} d^{-1} in the deeper 800 m trap (Fig. 3). Similarly high DA fluxes were observed in the SBB in May 2002 and February 2004, with DA fluxes exceeding 100,000 ng DA m^{-2} d^{-1} (data not shown). Note that for the SPB traps there is an inverse relationship between DA concentrations and fluxes due to the decline in sediment mass flux between 550 and 800 m. Therefore, although particles collected in the 800 m trap sometimes contained higher DA concentrations than in the 550 m trap, much less material was transported to the greater depth (lower mass flux), resulting in lower DA fluxes at 800 m. More frequent surface sampling (weekly rather than monthly) and larger spatial coverage (20 surface sampling locations compared with three) aided in the documentation of peak toxin concentrations during surface blooms in the SPB. *Pseudo-nitzschia* cell fluxes in the SBB sediment trap ranged from 19,700 to 76,100,000 cells m^{-2} d^{-1} (Fig. 2b).

The lack of a significant temporal lag between the surface concentration and deep flux observations suggests rapid vertical transport of significant numbers of *Pseudo-nitzschia* cells and associated DA. To investigate the correlations between surface concentrations and sediment-trap fluxes, surface and trap data were paired using observed settling velocities of 117–173 m d^{-1} for diatom aggregates in SBB (ref. 23). This is equivalent to a surface bloom requiring approximately 3 d to sink to the depth of the $SBB_{540\,m}$ and $SPB_{550\,m}$ traps and 5 d to reach the $SPB_{800\,m}$ trap. Applying these lags to regression analyses between DA concentrations in surface waters and sediment-trap DA fluxes revealed significant linear relationships in all three traps ($SBB_{540\,m}$, $n = 10$, $r^2 = 0.66$, $p < 0.01$; $SPB_{550\,m}$, $n = 11$, $r^2 = 0.82$, $p < 0.001$; $SPB_{800\,m}$, $n = 12$, $r^2 = 0.38$, $p < 0.05$). Surface–depth connectivity was also evident using a 3 d lag for the export of *Pseudo-nitzschia* cells to 540 m ($SBB_{540\,m}$, $n = 13$, $r^2 = 0.50$, $p < 0.01$). The coherence is particularly remarkable as the surface-water samples reflect single-day surface time points, whereas the sediment traps reflect integrated weekly to biweekly averages. This strong link further indicates that it may be possible to model DA transport to depth using only surface sampling.

Our findings are consistent with previous studies that suggest aggregation of diatom blooms during senescence increases particle sinking velocities[23], and that the siliceous cell walls of diatoms act as ballasting material facilitating the transport of organic matter to depth[24]. The rapid export of toxin-containing cells to depth minimizes the photodegradation of DA in the sunlit portion of the water column[6,7], slows down other unidentified degradation processes as colder deeper waters are reached and reduces the time period of DA leakage from senescent cells during sedimentation. DA is highly water soluble, and once it is released from the cells to the surrounding water[17] seems only minimally particle reactive[21,25]. DA molecules in sea water may also undergo conformational changes in structure that may affect toxicity[26]. However, DA packaged in rapidly sinking aggregates will reach

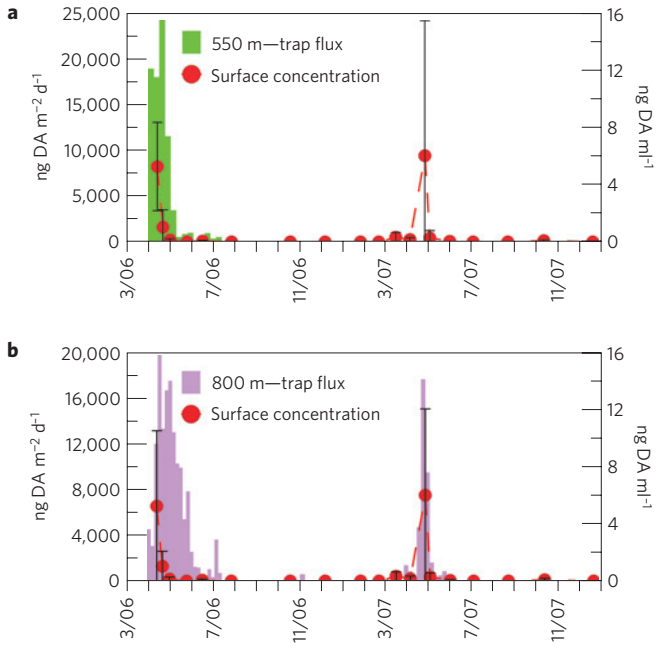

Figure 3 | Domoic acid in sediment-trap material and surface waters of San Pedro Basin. a,**b**, Comparison of surface DA concentrations with DA fluxes from sediment traps at 550 m (**a**) and 800 m (**b**) from March 2006 to January 2008. The bar width reflects the duration for which a trap cup was collecting. Surface concentrations are based on an average of 20 sampling stations, with errors bars reflecting one standard deviation. The May 2007 DA event is not present in the 550 m trap because the trap was not collecting material during this time period.

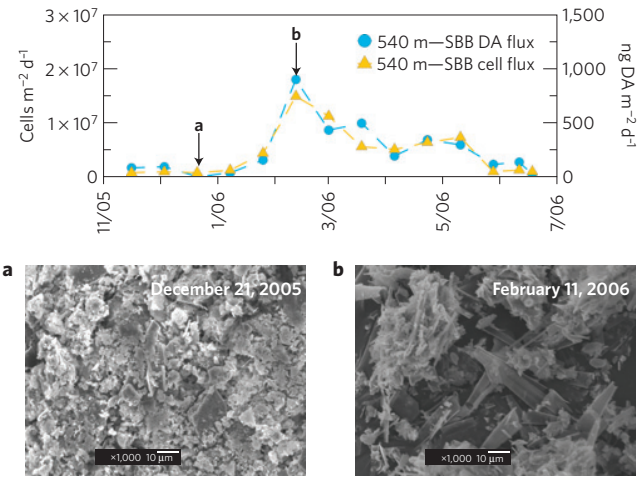

Figure 4 | Comparison of *Pseudo-nitzschia* bloom and non-bloom events. **a**,**b**, SEM images of non-bloom (**a**) and bloom (**b**) periods of *Pseudo-nitzschia* in sediment-trap material (540 m) collected in the SBB correspond to a toxic bloom as seen in the panel above. During SEM analysis *Pseudo-nitzschia australis*, a known toxin producer, was identified as the dominant *Pseudo-nitzschia* species from sediment traps at both study sites in 2006 and from SPB traps in 2007.

the benthos quickly and be readily available for bioaccumulation. Light microscopy confirms that a significant proportion of the *Pseudo-nitzschia* frustules found in the SBB and SPB traps were intact, containing pigment and even maintaining their chain form (not pictured). Scanning electron microscopy (SEM) images of unground freeze-dried sediment trap material enabled *Pseudo-nitzschia* species identification and also illustrated the difference between non-bloom and bloom conditions (Fig. 4).

Peaks in surface DA concentrations and *Pseudo-nitzschia* cell abundances with sediment-trap flux measurements occasionally differed in their relative magnitudes, or were offset by one to two weeks. In SBB, this was probably due to the timescale and low spatial coverage of the surface data as well as the complex hydrography of the basin[27]. The presence of a persistent mesoscale eddy during August–September 2005 may explain the October 2005 spike in *Pseudo-nitzschia* cell flux. The eddy acted as a spatial integrator owing to its convergent centre, thus maximizing the potential for marine flocculation, especially on relaxation of the eddy. Fluxes to the 800 m trap in SPB during April 2006 continued for several weeks after the decline of the surface bloom, with high fluxes not reflected in the shallower 500 m trap. Some of the flux at 800 m may be due to advection of material off the shelf in nepheloid layers between 550 and 800 m or more rapid chemical decomposition in the shallower trap. The offset from surface concentrations may also reveal the presence of a subsurface *Pseudo-nitzschia* bloom[28], which would not have been detected in the 0–1 m water sampling. Regardless, comparison of cell abundances and DA in surface samples and at depth clearly demonstrates that the growth and vertical transport of DA-containing *Pseudo-nitzschia* cells was tightly coupled. Furthermore, the observed DA sediment-trap fluxes should be considered conservative estimates, because particulate fluxes probably decrease with increasing water depth[3]. Thus, shallower benthic communities are more likely to receive larger amounts of DA after bloom demise than we observed.

To the best of our knowledge, this study is the first to document the incorporation of DA into bottom sediments, although others have reported *Pseudo-nitzschia* cells present in sediments[5]. Analysis of 11 surficial (0–0.25 cm) sediment samples retrieved from the SBB sediment-trap site (2005; 590 m water depth) and within the SPB area on the Palos Verdes Shelf (2001, 2003 and 2005; 60–70 m water depth) revealed values of 19 ng DA per g dry sed. wt and from less than 17 to 38 ng DA per g dry sed. wt, respectively (Fig. 1). Although the dataset is small, this provides evidence that DA reaches the seafloor and may be preserved long after a toxic bloom event occurs.

It is important to understand the environmental conditions favouring the formation of *Pseudo-nitzschia* blooms, the triggers for the production of the neurotoxin DA and the ultimate fate of the toxin produced in surface waters, for the protection of human and coastal health. This study is the first to provide evidence for the rapid vertical transport of DA-containing *Pseudo-nitzschia* cells to significant depths below the euphotic zone. The resulting high vertical flux of DA to depth indicates that these particles are efficient vectors for the bioaccumulation of DA within mesopelagic and benthic food webs. Our data further confirm that DA-laced sinking particulates are incorporated into underlying sediments, where they are available for consumption and incorporation into bottom feeders after the demise of a *Pseudo-nitzschia* bloom. Harmful algal blooms, including those dominated by *Pseudo-nitzschia* spp., are expected to increase in frequency and expand in their geographical range[3]. A thorough understanding of the transport and fate of toxin-loaded cells is thus essential for evaluating their adverse effects on marine ecosystems and addressing the human-health issues associated with trophic food-web interactions.

Methods

Domoic acid analysis. SBB sediment-trap DA measurements with LC-MS/MS were made on trap solutions (stored in dark, 4 °C) and 50% methanol extractants of dried, ground quarter-splits of trap particulates and surface-core samples. DA analysis[21] was carried out with an Agilent 1100 high-performance liquid chromatograph coupled to a Micromass-Quattro mass spectrometer equipped with an electrospray ion-spray interface. Modifications to this method included a sample injection of 20 µl and timing adjustments to the applied reagent gradient. Detection limits on trap and core extractants were 1.3 ng DA ml^{-1}, which corresponded to 34

and 17 ng DA per g dry sed. wt respectively. It was assumed that dissolved DA found in trap solutions resulted from leaching of trap particulates. Therefore, DA concentrations were calculated as the sum of the two (volume-corrected) fractions. For the SPB, aliquots from wet splits of the sediment-trap material were analysed using ELISA (ref. 15; ELISA kits, Biosense Laboratories, Bergen, Norway). Detection limits were 0.01 ng particulate DA ml^{-1} and 100 ng DA per g dry sed. wt. Comparisons between LC-MS/MS and ELISA agreed within a standard deviation of ±18.5 to 52.2% (average 31.6%, $n = 4$). DA fluxes at both sites were calculated from the product of DA concentration (ng DA per g dry wt) and total mass flux ($g\,m^{-2}\,d^{-1}$). Whole-water samples were collected at all surface sites and filtered to determine particulate DA concentrations in both SBB (ref. 22) and SPB (ref. 15). DA standards were purchased from the Certified Reference Materials Program at the National Research Council of Canada Institute for Marine Biosciences (Halifax, Nova Scotia, Canada).

***Pseudo-nitzschia* analysis.** Whole-water samples were collected from SBB (ref. 22) and SPB (ref. 15) and preserved for *Pseudo-nitzschia* cell counts. SBB trap samples were prepared for cell counts by resuspending unground freeze-dried material in deionized water. Cell enumeration was based on standard settling techniques and the Utermöhl method for inverted light microscopy[29]. SEM was used for selected SBB samples to determine *Pseudo-nitzschia* species using a desalinization and freeze-dry approach.

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Author contributions

E.S.-W., A.S. and C.R.B.-N. measured DA concentrations, conducted *Pseudo-nitzschia* cell counts and handled data interpretation for the SBB and SPB datasets. J.M.B. and J.L.F. helped in the development of the LC-MS/MS method for SBB. S.L.M. provided SEM images. C.A. provided surface DA and *Pseudo-nitzschia* cell concentrations for SBB. E.F. measured DA with ELISA kits on SPB samples. R.S. and I.C. assisted sampling collection throughout the covered time period in the SPB area. R.T. and W.M.B. provided sediment-trap samples in SBB and SPB, respectively. D.A.C., B.H.J., P.E.M. and D.A.S. provided support and infrastructure for the SPB *Pseudo-nitzschia* and DA measurements.

Additional information

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