2021-09-15

Inorganic nitrogen and phosphorus in Western European aerosol and the significance of dry deposition flux into stratified shelf waters

White, C

10.1016/j.atmosenv.2021.118391
Atmospheric Environment
Elsevier BV

Inorganic nitrogen and phosphorus in Western European aerosol and the significance of dry deposition flux into stratified shelf waters

Caroline White[1], Simon J. Ussher[1], Mark F. Fitzsimons[1], Sov Atkinson[1], E. Malcolm S. Woodward[2], Mingxi Yang[2], Thomas G. Bell[2]

[1] Biogeochemistry Research Centre, School of Geography, Earth and Environmental Science, University of Plymouth, Drake Circus, Plymouth, PL4 8AA, UK

[2] Plymouth Marine Laboratory, Prospect Place, Plymouth, PL1 3DH, UK

ABSTRACT

Dry deposition of nitrogen (N) and phosphorus (P) from the aerosol phase represents a potential source of nutrients to marine surface waters. To investigate the significance of this deposition pathway, aerosol samples were collected from Penlee Point Atmospheric Observatory in SW England, UK, over a 6-month period (February to July 2015) covering the spring bloom. Samples were analysed for nitrate, ammonium and phosphate and the dry deposition flux of these nutrients calculated to assess its potential impact on primary production in nearby surface seawater. Aerosol-derived N and P deposition fluxes ranged from 2.7 - 620 µmol N m^{-2} d^{-1} and 0.16 - 1.6 µmol P m^{-2} d^{-1}, respectively. Air mass back trajectory analysis indicated that the highest N fluxes were associated with polluted European air masses, highlighting a significant anthropogenic influence on N-content of aerosols. The N:P ratios of aerosol fluxes and water column concentrations indicated that P deposition was unlikely to be biologically significant in the region. In contrast, aerosol deposition was a significant episodic source of new N to marine phytoplankton after the onset of water column stratification. Carbon fixation estimates indicated that the maximum proportion of new primary production sustained by aerosol-N deposition was 22.4 %, a factor of ten higher than the study average. These data suggest

that enhanced N-deposition from polluted continental air masses could sustain pulses of surface ocean biological productivity during periods of dissolved N depletion.

1. INTRODUCTION

Reactive nitrogen (N) and phosphorus (P) are vital macronutrients in surface seawater, fuelling primary production by marine phytoplankton and the biological carbon pump (Elser *et al.*, 2007). Anthropogenic activities in the last century have created new sources of reactive N and significantly altered the global nitrogen cycle (Duce *et al.*, 2008; Galloway *et al.*, 2003; Martino *et al.*, 2014). Emission model studies estimate a fourfold increase in inorganic nitrogen emissions since 1850 (Duce *et al.*, 2008; Jickells *et al.*, 2017; Krishnamurthy *et al.*, 2009). The Redfield ratio of N to P uptake (16:1) in phytoplankton means that small changes to the P pool can impact the N:P ratio if the system is close to Redfield (Elser *et al.*, 2007).

Atmospheric reactive N is made up of inorganic oxidised forms (nitrate, NO_3^-, and nitrite, NO_2^-), and the inorganic reduced form, ammonia/ammonium (NH_3/NH_4^+), as well as an organic N fraction (Hertel *et al.*, 2012). Atmospheric reactive N in the aerosol phase can be transported long distances from emission sources, potentially spanning continents and ocean basins. From the perspective of primary production, approximately 70% of the surface ocean is N limited or N co-limited with P (Moore *et al.*, 2013). Atmospheric deposition can introduce significant pulses of reactive N to N-limited surface waters (Kim *et al.*, 2014; Okin *et al.*, 2011; Owens *et al*., 1992).

Anthropogenic emissions of oxidised N are primarily derived from N oxides from combustion processes such as road transportation, shipping and industry (Hertel *et al.*, 2012; Okin *et al.*, 2011). A large proportion of gas phase N oxides (NO_x) undergo atmospheric transformation to form nitric acid, which displaces chloride on the surface of sea salt particles (typically coarse mode, >1 μm diameter) in the marine boundary layer (Ottley & Harrison, 1992; Yeatman, Spokes & Jickells, 2001). Emissions

of reduced N are predominately from agricultural sources, as well as from biomass burning (Hertel *et al.*, 2012; Okin *et al.*, 2011). Gas phase NH_3 is very soluble and readily protonates in the aqueous phase of the aerosol to form the NH_4^+ ion. Nitric acid also reacts with NH_3 to form fine mode (<1 μm diameter) ammonium nitrate aerosol (Yeatman, Spokes & Jickells, 2001).

Jickells *et al.* (2017) estimated global inorganic nitrogen emissions as ca. 100 Tg N yr^{-1}. Reactive N emission estimates for Europe were reported by Leip *et al.* (2011): NO_x emissions totalled 3.5 Tg N yr^{-1} and were dominated by road transport (1.3 Tg N yr^{-1}) and combustion from industry (1.0 Tg N yr^{-1}). Reduced N (NH_3/NH_4^+) emissions totalled 3.2 Tg N yr^{-1} and were dominated by agriculture at 3.0 Tg N yr^{-1} (Leip *et al.*, 2011). Hence, the emission ratio of oxidised and reduced N species both in Europe and globally is estimated to be approximately 1:1 even though the sources are not the same.

Phosphorus is mainly emitted to the atmosphere as aerosol (Myriokefalitakis *et al.*, 2016). The principal sources include mineral dust (48 %), anthropogenic (14 %) and biogenic emissions (34 %; from plants, animals and bacteria). Total P in the atmosphere predominately comprises insoluble mineral dusts, orthophosphates, soluble and insoluble organic P (Myriokefalitakis *et al.*, 2016). Orthophosphate (PO_4^{3-}) is the most common and bioavailable form of soluble P in the ocean (Björkman & Karl, 2003; Mahowald *et al.*, 2008). Mahowald *et al.,* (2008) estimated that 0.74 Tg of PO_4^{3-} is released to the atmosphere each year across the globe. These global estimates, which are derived from a wealth of past measurements, e.g. Baker *et al.,* (2006; 2007; 2010; 2017), suggest that anthropogenic activity has not significantly altered aerosol PO_4^{3-} concentrations. Based on the global estimates for N and P emissions (Jickells *et al*., 2017; Mahowald *et al*., 2008) the global atmospheric N:P ratio is greater than 400, hence it can further be concluded that globally the aerosol phase is N rich compared to P.

Atmospheric deposition can provide an important additional source of soluble N to marine surface waters under certain conditions. Previous studies observed several significant N deposition events from air masses originating from Europe and estimated that N deposition could support up to 30 % of

new daily primary production in the NE Atlantic Ocean (Spokes *et al.,* 2000; Spokes and Jickells, 2005). In seasonally stratified waters during the spring/summer months, water column stratification can trap nutrients within a limited depth range in the sunlit euphotic zone, which facilitates phytoplankton growth but can also isolate them from remineralised nutrient sources at depth. Sustained biological activity draws down available nutrients to the point where external inputs of N (e.g. from atmospheric deposition) have the potential to be highly significant (Chester & Jickells, 2012; Spokes & Jickells, 2005; Spokes *et al.*, 2000; Owens *et al.,* 1992). However, it must be noted that stratification within the water column is a dynamic feature which varies in depth and can even be broken down by strong physical processes (e.g. winds, currents). A complete breakdown in stratification allows nutrients trapped in the deep shelf water to be mixed throughout the water column, thus resupplying the surface with nutrients, including bioavailable N and P (Schmidt *et al*., 2020; Maier *et al*., 2012; Lentz *et al*., 2003).

Carbon flux and carbon fixation measurements in coastal and shelf regions, during seasons with active primary production, have shown that wet and dry deposition of N can contribute 0.4 – 3.7 % of new primary production (Park *et al*., 2019; Kocak, 2015; Singh *et al*., 2012). Even in regions of significant wind driven upwelling such as the Californian coastline, atmospheric N-deposition is estimated to account for up to 8 % of new productivity (Mackey *et al*., 2010). The largest impact of atmospheric N deposition has been found in regions of high population density and air pollution. In the SE China coastline, 5.6 – 19.4 % of new primary production is supported by N-deposition from nearby anthropogenic sources during winter and summer seasons (Wang *et al*., 2019). These studies demonstrate that increased inputs of reactive nitrogen to coastal regions from anthropogenic sources will have significant impact on coastal marine primary production in the future, as predicted by several global modelling studies (Duce *et al*., 2008; Baker *et al*., 2017).

The aim of this study was to integrate atmospheric aerosol and marine nutrient observations at a well-studied coastal time-series site in order to estimate the impact of atmospheric reactive soluble N and P deposition on seasonally stratified shelf waters. The study site is situated on the south-west coast

of England, UK, and uses atmospheric time-series data from Penlee Point Atmospheric Observatory (PPAO) and seawater time-series data from the Western Channel Observatory (WCO). The data were collected between February and July 2015, spanning the period of water column stratification and the phytoplankton spring bloom.

2. METHODS

Atmospheric data were collected from the PPAO, situated on the Rame Head Peninsula on the western edge of Plymouth Sound, Cornwall, UK (50°19.080 N, 4°11.350 W). The coastal site is exposed to a number of distinct wind sectors/air masses, including the North Atlantic Ocean from the southwest, and mainland Europe/ship emission within the English Channel from the east/southeast (Figure 1). The PPAO was established in 2014 by Plymouth Marine Laboratory (PML) in collaboration with the University of Plymouth and detail on the site characteristics is presented elsewhere (Yang *et al.,* 2019; Yang *et al.*, 2016a; Yang *et al.*, 2016b). Gas phase carbon dioxide, methane, sulfur dioxide, ozone and meteorological variables (wind speed, wind direction, relative humidity, atmospheric pressure and rain rate) are continuously monitored. Aerosol samples were collected weekly and analysed at the University of Plymouth (UoP) for inorganic nutrients.

Seawater samples and data were collected from L4, a long-term coastal monitoring buoy located 6 km south of PPAO (50°15.00' N, 4°13.02' W). L4 is a key sampling station for the Western Channel Observatory (WCO, http://www.westernchannelobservatory.org.uk). Continuous measurements at the L4 buoy include PAR, sea surface temperature, salinity and chlorophyll. Routine weekly water column samples are collected from L4 for nutrient concentrations (NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}), (Woodward & Harris, 2019), and are analysed in a shore-based laboratory by a SEAL Analytical segmented flow autoanalyzer using colorimetric analysis techniques (Woodward & Rees, 2001). Concurrent temperature and salinity profiles are collected weekly by CTD from the RV Plymouth Quest.

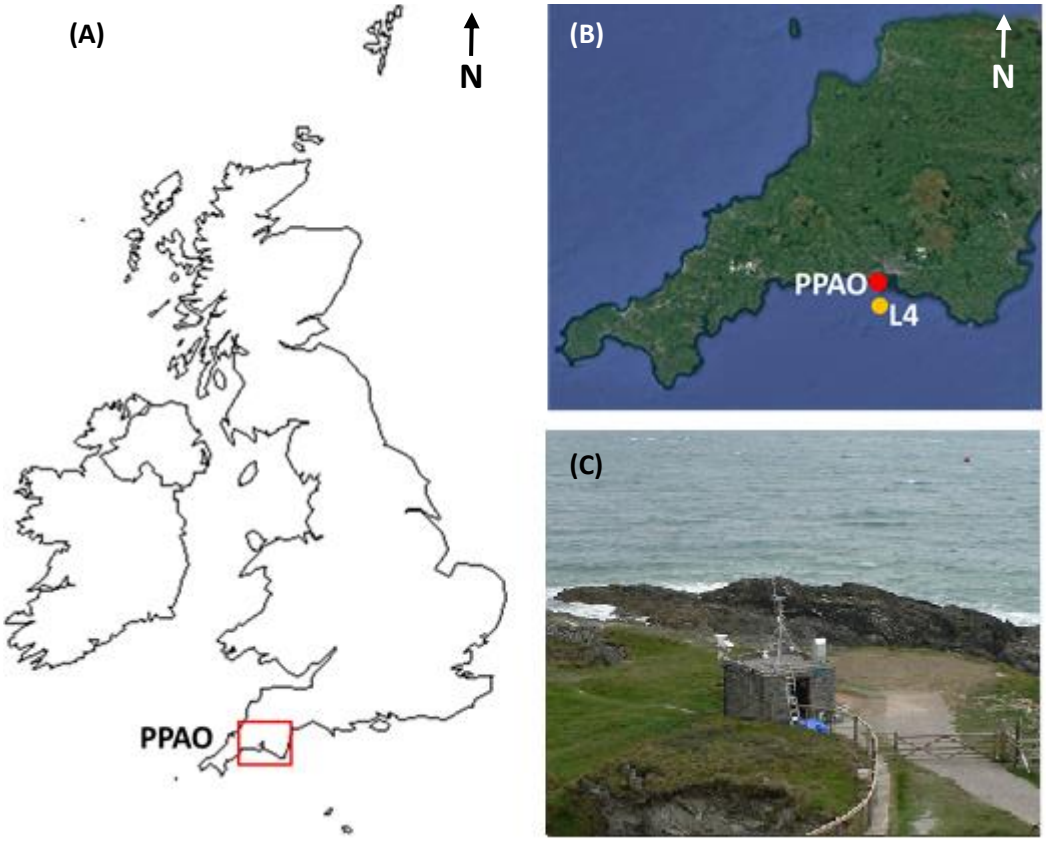


Figure 1: *(A) Location of study area. (B) Location of Penlee Point Atmospheric Observatory (PPAO) and of the Western Channel Observatory marine time series L4 station/buoy. (C) Site in Spring 2015 (photo taken facing south). Aerosol samples were collected from a Hi-Vol sampler positioned on the SW corner of the roof of the building.*

Aerosol Sampling and Analysis

Particulate aerosol samples were collected onto acid-cleaned and combusted 8 x 10" (203 x 254 mm) Whatman Quartz Microfiber Filters (QMA) using a Tisch Environmental (model TE-5170) high-volume aerosol sampler (approximately 1 m^3 min^{-1} flow rate), which was calibrated in accordance with the product handbook using a manometer once a month. Samples (n = 22) were collected weekly from 9th February to 14th July 2015. Filters were pre-loaded into an aluminium filter cassette for sampling and

protected by an aluminium cover until sampling began. There was a sampling gap from 5th-26th March due to a sampler malfunction. During the sampling days, air was filtered for either 24 hours (9th February-9th April) or 12 hours (9th April-14th July). Filter samples were collected and sealed in zip-lock bags, then transported in an insulated container for storage (-20 °C freezer) and analysis at the UoP laboratory. Aerosol filters samples were prepared for analysis by subsampling into quarters and submerging one subsample in 125 mL of high purity water (HPW; ≥ 18.2 MΩ cm) overnight to leach the soluble N and P into solution (Cornell & Jickells, 1999). Leaching efficiency was assessed by performing a second extraction on sub-samples. All analytes of secondary extractions were below the limit of detection, confirming high efficiency of the initial single extraction.

Aerosol NO_2^-, NO_3^- and PO_4^{3-} were determined by spectrophotometric analysis based on Hansen and Koroleff, (2007) and Gardolinski *et al.,* (2001), using a continuous flow, air-segmented nutrient auto analyser (Skalar SAN^{plus} series 1074). Instrumental precision was determined from the relative standard deviation (RSD) of triplicate measurements. Mean RSD for NO_3^- + NO_2^- was 2.84 % (n = 22), and for PO_4^- was 1.34 % (n = 22), which is consistent with inter-comparison studies involving the same instrument (Birchill *et al*., 2019). Concentrations of NO_2^- for aerosols are typically below detection limits (approx. 0.1 nmol m^{-3}: Baker *et al.*, 2010; Lesworth, Baker & Jickells, 2010), so this small fraction (< 4% maximum: 0.2% median) was combined with NO_3^- and reported as aerosol NO_3^-. Ammonium (NH_4^+) was analysed by fluorimetry, using a Hitachi F-4500 fluorometer (see Holmes *et al.,* 1999). Air concentrations were calculated by dividing the detected values by the total volume of air that had passed through the filter.

Dry Deposition Fluxes

Dry deposition fluxes were calculated to investigate the importance of aerosol as a source of nutrients to coastal waters (Spokes & Jickells, 2005). Here, fluxes are calculated as daily (24 h) inputs, hence the airmass concentrations collected over a 12 h period have been interpolated as a constant 24 h

concentration. The deposition flux (Equation 1) is the product of the aerosol concentration (C) and the deposition velocity (V_d):

$$Flux = C\ V_d \quad (1)$$

The deposition velocity is influenced by physical processes such as gravitational settling, impaction and diffusion, which are constrained by particle size, wind speed and sea surface conditions (Duce *et al.*, 1991). The deposition velocity is not well quantified (Baker *et al.,* 2010; Duce *et al.*, 1991) and there is a large uncertainty on current estimates. We used a particle size-dependent V_d value: 2.0 cm s^{-1} for coarse mode particles (diameter > 1 µm) and 0.1 cm s^{-1} for fine mode particles (diameter < 1 µm) (Duce *et al.*, 1991; Slinn & Slinn, 1980). These V_d values were chosen to enable comparison with other studies (e.g. Spokes & Jickells, 2005; Yeatman *et al.*, 2001).

Samples collected from PPAO were not size-segregated, so it was necessary to estimate the relative distribution of NO_3^-, NH_4^+ and PO_4^{3-} within the fine and coarse mode aerosol. PO_4^{3-} sources predominantly generate larger sized (> 1 µm) aerosols, with the exception of combustion sources which can either be greater or less than 1 µm (Myriokefalitakis *et al.*, 2016; Mahowald *et al*., 2008). Combustion sources represent approximately 14 % of global aerosol PO_4^{3-} (Mahowald *et al*., 2008), so we assume that all aerosol PO_4^{3-} was in the coarse mode and apply a deposition velocity of 2.0 cm s^{-1}, appropriate to >1µm particle sizes to calculate the deposition flux (Duce *et al.*, 1991). Defining size distributions for NO_3^- and NH_4^+ is more challenging as previous studies have shown that coarse and fine mode ratios of NO_3^- and NH_4^+ are highly dependent on source region (Bencs *et al.*, 2009; Spokes & Jickells, 2005; Yeatman *et al.*, 2001). PPAO is situated between two well- established atmospheric observatories, Mace Head, Galway (Ireland) and Weybourne, Norfolk (UK). Mace Head and Weybourne are exposed to the same air mass sectors described at PPAO and size segregated NO_3^- and NH_4^+ measurements have been made for these sectors (Spokes & Jickells, 2005; Yeatman *et al.*, 2001). We used the Mace Head and Weybourne data (Table 1) to estimate the size distribution of NO_3^- and

185 NH_4^+ in the air masses encountered at PPAO for this study. The uncertainty related to this estimation
186 has been taken into account in any discussion of fluxes.

187 **Table 1:** Percentage medians (± range) of coarse mode (> 1µm) NO_3^- and NH_4^+ found in aerosols from
188 source region extrapolated from Spokes & Jickells (2005) and Yeatman *et al* (2001).

Source Region	**> 1µm NH_4^+**	**> 1µm NO_3^-**
N Atlantic Clean	18.5 % (± 17.5%)	70 % (± 21 %)
N Atlantic Mixed	20.5 % (± 5.5)	65 % (± 12 %)
Channel Mixed	36.5 % (± 0.5 %)	69 % (± 1 %)
Continental	43.5 % (± 1.5 %)	48.5 (± 8.5 %)

189

190 **Source Region Analysis**

191 Wind sectors have been defined previously for PPAO using the local wind direction (Yang *et al.*, 2016a).
192 In this study, we combined the local wind direction with air mass back trajectory analysis to categorise
193 the source region of each aerosol sample. Air mass back trajectories were calculated using the
194 National Oceanic and Atmospheric Administration (NOAA) HYbrid Single-Particle Lagrangian
195 Integrated Trajectory (HYSPLIT) model (http://ready.arl.noaa.gov/HYSPLIT.php). A back trajectory was
196 calculated every 6 hours while the aerosol sampler was running, resulting in 3 trajectories for 12 hour
197 samples and 6 trajectories for 24 hour samples. Trajectories were initiated at 20 m above ground level
198 and run backwards for 72 hours.

199 Each sample was classified into one of four air mass source regions using the local wind speed and
200 direction (Yang *et al.*, 2016a) and its HYSPLIT back trajectory. The four wind sectors are the
201 Continental, North Atlantic, Channel Mixed and N Atlantic Mixed (see examples in Figure 2). The
202 predominant wind direction at PPAO is from the West/South-West, and the North Atlantic Ocean is
203 the dominant influence on this air (North Atlantic). Air from the West and North-West often originates

over the North Atlantic, but has spent time over Ireland and rural parts of the UK prior to reaching the PPAO (N Atlantic Mixed). Winds from the East/South-East have been influenced by ship emissions in the English Channel and anthropogenic/terrestrial emissions from continental Europe (Continental). During low wind speed events, the air tends to stagnate in the local area, picking up a mixture of ship and marine emissions (Channel Mixed).

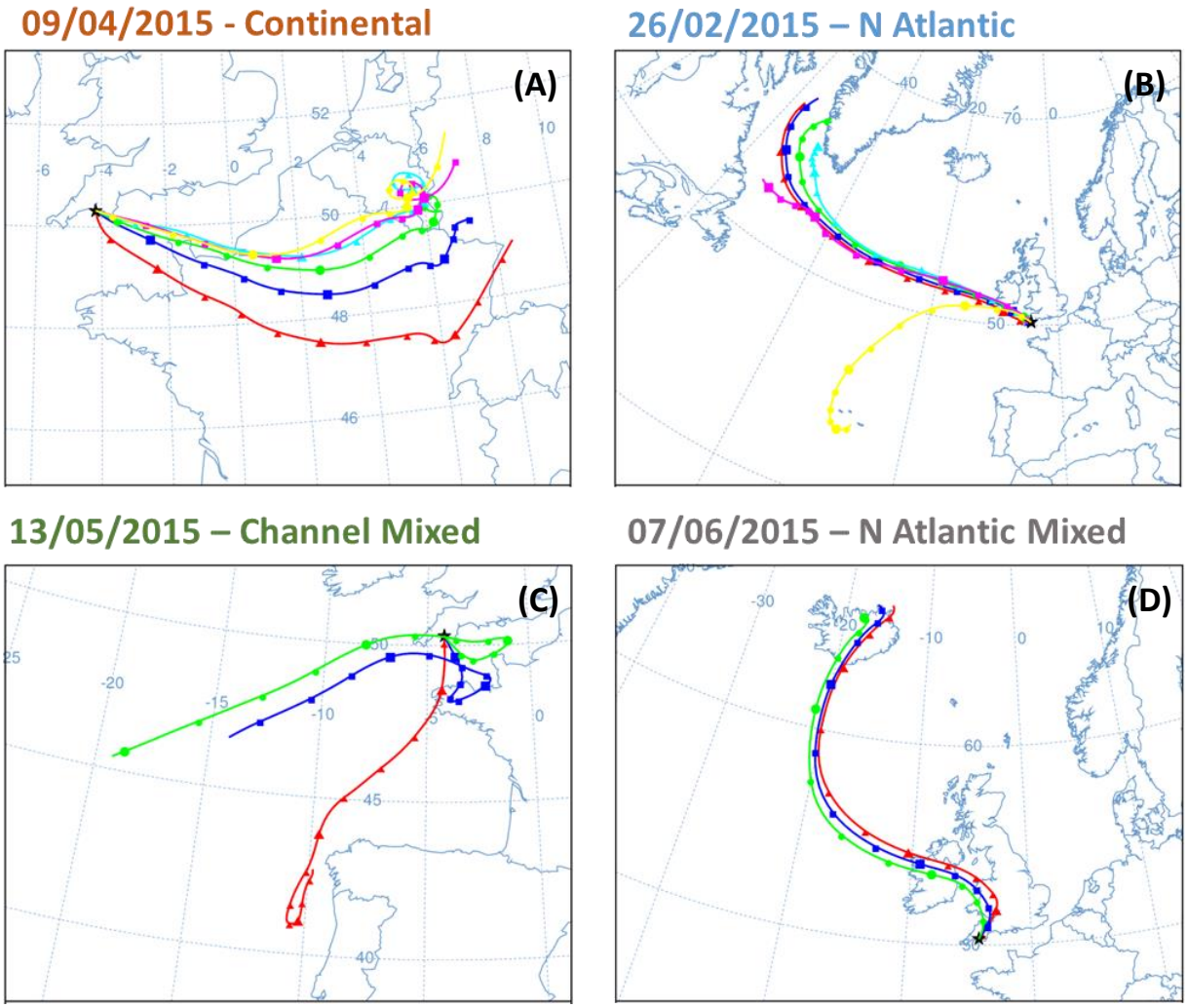


Figure 2: *Example back trajectories for the four sectors defined for this study. Multiple trajectories were run per sample (different colour lines). Symbols represent 6 hour intervals along the trajectory.*

3. RESULTS

3.1 Penlee Point Atmospheric Observatory Aerosols

Air mass NO_3^- concentrations varied from 2–366 nmol N m^{-3}, with the minimum and maximum occurred on 26th February and 9th April, respectively (Figure 3; Figure 4). The highest aerosol NO_3^- concentrations were observed in air masses from continental Europe/UK Mainland, and these were associated with an easterly local wind direction (Figure 4). NO_3^- concentrations associated with this source region also had the greatest concentration range (128 – 366 nmol N m^{-3}). In contrast, low aerosol NO_3^- concentrations were observed in North Atlantic clean aerosols (2–27 nmol N m^{-3}) except on the 16th June (43 nmol N m^{-3}). Low wind speeds prevailed during sample collection on the 16th June, and the back trajectory suggests that the air mass circulated over the Celtic Sea and English Channel. Hence it is likely this aerosol sample had entrained emissions from the intense shipping activity in these waters.

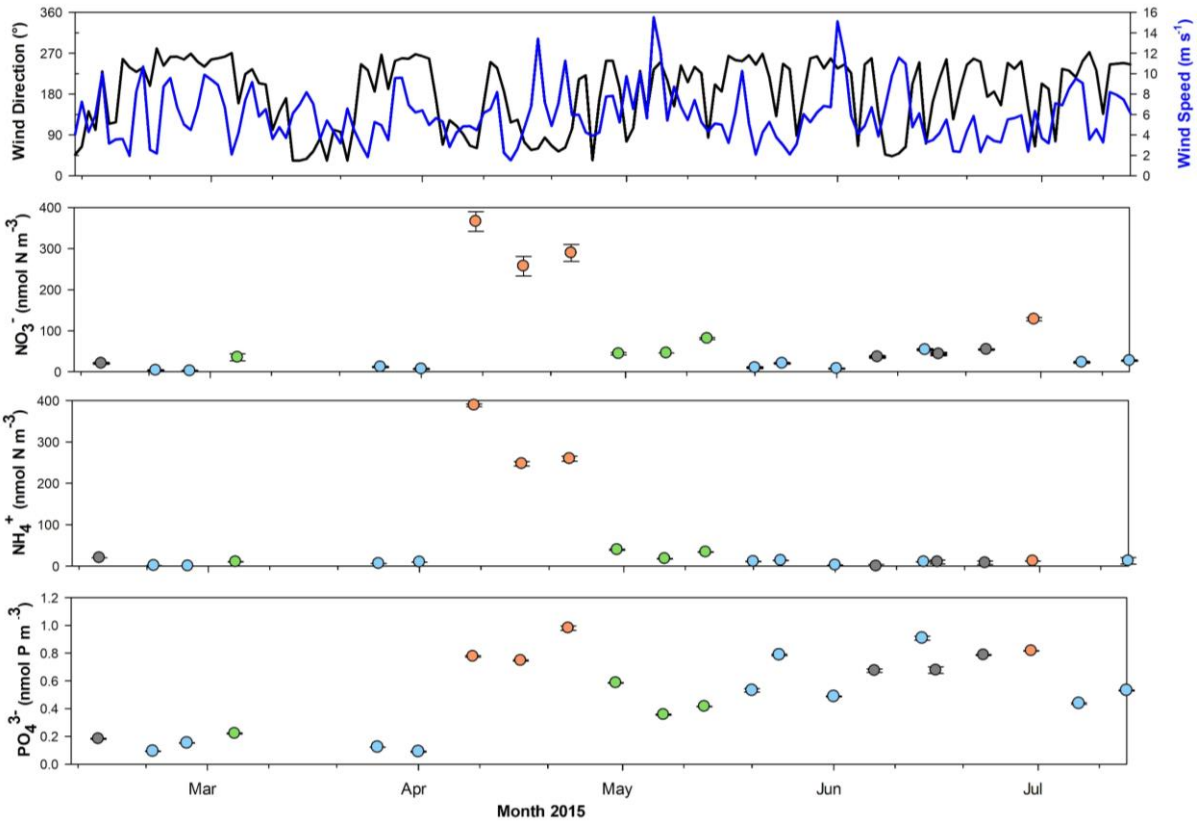


Figure 3: *Timeseries of aerosol inorganic N (NO_3^- and NH_4^+, nmol N m^{-3}) and PO_4^{3-} (nmol P m^{-3}) concentrations, wind speed (m s^{-1}) and local wind direction (degrees) between 9th February and 14th July 2015. Points are coloured by source region classification: North Atlantic Clean (blue), Continental*

(orange), Channel Mixed (green) and North Atlantic Mixed (grey). Major tick marks represent the 1st of the month and minor tick marks represent 10th and 20th days.

Aerosol NH_4^+ concentrations ranged from 0.21 – 389 nmol N m^{-3} and tended to co-vary with NO_3^- concentrations (Figure 3). Continental aerosols had the highest NH_4^+concentrations. One exception was on 30th June 2015, when NH_4^+ concentrations were 12.2 nmol N m^{-3}, which is more comparable with background North Atlantic samples than with other Continental samples. The NO_3^- concentration in the same sample was approximately 50% of the other three Continental samples. Back trajectory analysis shows that the air had circulated in the English Channel for 72 hours prior to sampling.

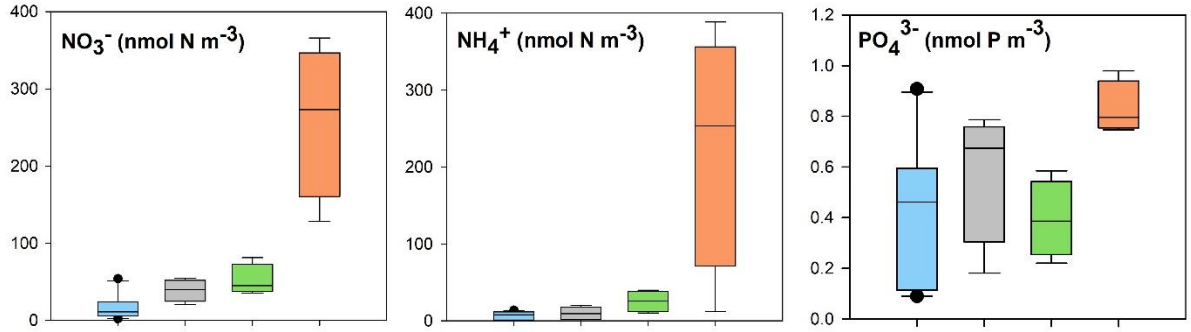


Figure 4: *Box and whisker plots of aerosol NO_3^-, NH_4^+ and PO_4^{3-} concentrations, coloured by source region classification: North Atlantic clean (blue, 10 samples), Continental (orange, 4 samples), Channel Mixed (green, 4 samples) and North Atlantic Mixed (grey, 4 samples).*

Aerosol phosphate (PO_4^{3-}) concentration ranged from 0.1 – 1.0 nmol P m^{-3}. The lowest concentrations were recorded on 21st February and 1st April 2015, and the highest occurred on 23rd April (Figure 4). PO_4^{3-} was considerably less abundant than aerosol nitrogen, and there was no clear link between the PO_4^{3-} concentrations and air mass classification or variations in inorganic nitrogen concentration. Mineral and soil dusts are the major source of soluble P for aerosol. These are typically larger particles with short atmospheric residence times. Thus, atmospheric P concentrations are likely to be dependent on localised continental sources rather than long range transport (Myriokefalitakis *et al.*,

2016). Average (mean and median) aerosol PO_4^{3-} concentrations in air masses from the European Continent/UK were elevated (Figure 4) compared to other source regions, especially North Atlantic Clean and Channel Mixed. Concentrations from the North Atlantic Mixed region were also slightly elevated, suggesting terrestrial influence as the trajectories passed over South West England and South East Ireland.

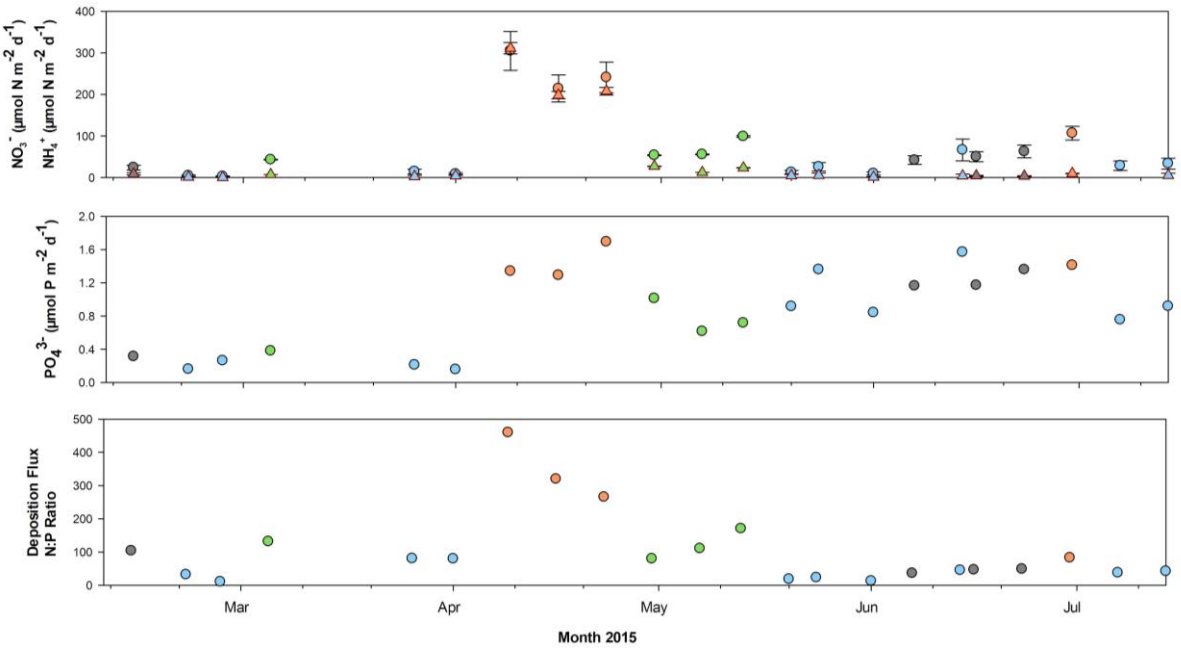


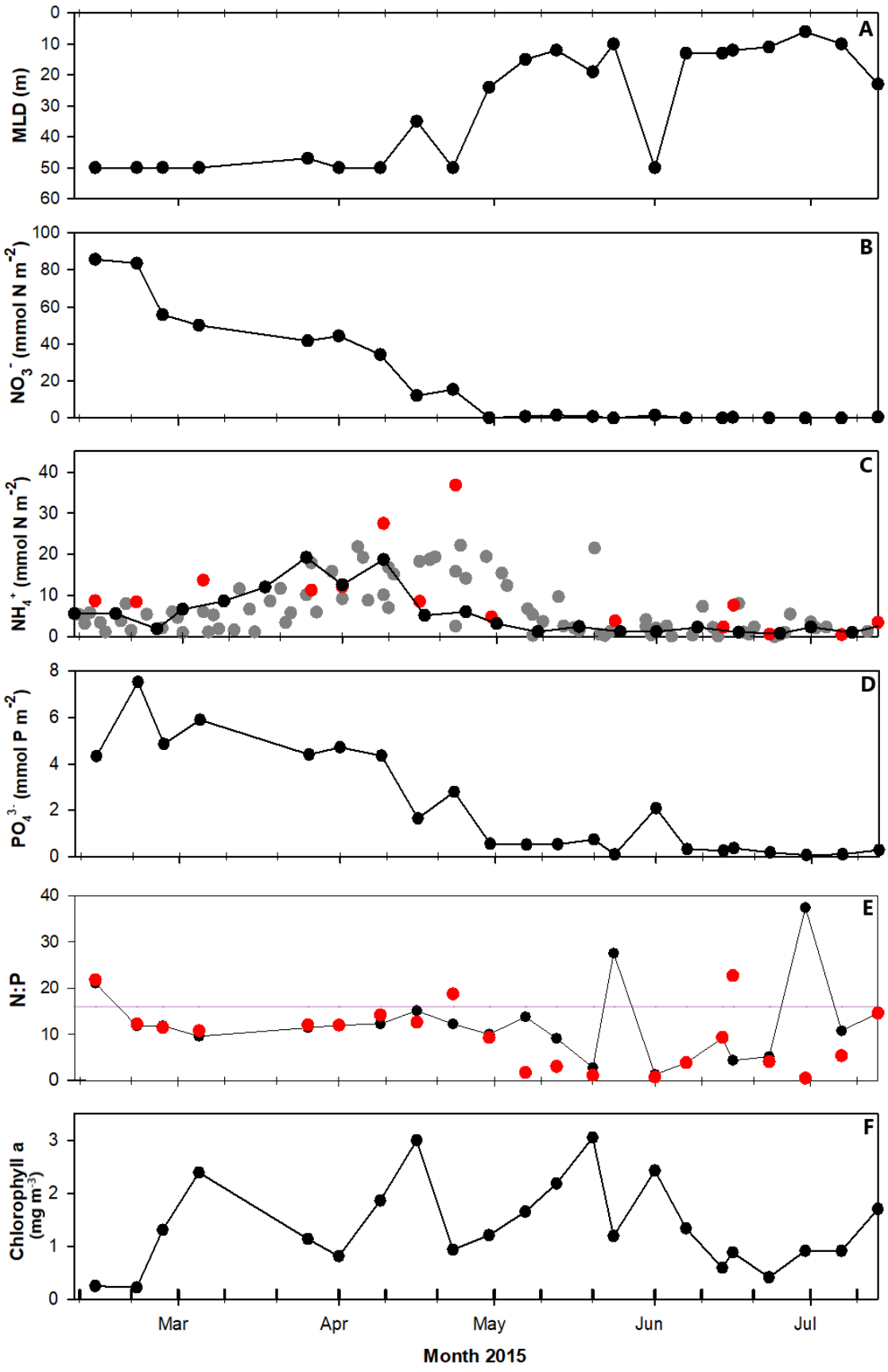
Figure 5: *Dry deposition fluxes for NO_3^-, NH_4^+ and PO_4^{3-} (µmol N/P m^{-2} d^{-1}) and the N:P ratio of the aerosol depositing on the sea surface. Circles and triangles in the top panel represent nitrogen fluxes resulting from NO_3^- and NH_4^+ respectively. Points are coloured by back trajectory source regions: North Atlantic Clean (blue), Continental (orange), Channel Mixed (green) and North Atlantic Mixed (grey). Error bars on NO_3^- and NH_4^+ show the maximum/minimum deposition using the coarse/fine size distribution ranges in Table 1. Major tick marks represent the 1st of the month and minor tick marks represent 10th and 20th days.*

Average NO_3^- and NH_4^+ deposition flux were 68 (± 12) and 38 (± 3) µmol N m^{-2} d^{-1} respectively. Deposition fluxes ranged from 3 (± 1) to 300 (± 47) µmol N m^{-2} d^{-1} for NO_3^- and 0.01 (± 0.03) to 310 (±14) µmol N m^{-2} d^{-1} for NH_4^+. The N:P ratio of the aerosol deposition flux (Figure 5) demonstrates that

N deposition far exceeds P deposition, with most samples exceeding 50:1 N:P ratio. Only 1 sample period had an N:P ratio in the deposited aerosol that fell below the Redfield ratio in seawater (16:1) .

3.2 Trends in marine mixed layer nutrients in the Western English Channel

Vertical nutrient profiles from the Western Channel Observatory L4 marine time series site were integrated down to the base of the spring/summer mixed layer. A pycnocline formed during spring from May onwards, and the average depth was 16 m (± 11 m). A mixed layer depth was defined for each profile using a ± 0.03 kg m^3 density difference starting at 3 m. Nutrient profiles were integrated down to the seabed (54 m) prior to stratification (Figure 6).


A
MLD (m)
0
10
20
30
40
50
60
B
NO_3^- (mmol N m^{-2})
0
20
40
60
80
100
C
NH_4^+ (mmol N m^{-2})
0
10
20
30
40
D
PO_4^{3-} (mmol P m^{-2})
0
2
4
6
8
E
N:P
0
10
20
30
40
F
Chlorophyll a (mg m^{-3})
0
1
2
3
Mar
Apr
May
Jun
Jul
Month 2015

272

Figure 6: *WCO L4 timeseries for spring bloom period in 2015. (A) Mixed layer depth used for nutrient integration, derived as +/- 0.03 kg m^{-3} from density profiles calculated from CTD temperature & salinity profiles (1 atm) starting at 3m. (B, C, D) Integrated mixed layer nutrient concentrations (NO_3^-, NH_4^+, PO_4^{3-}), (E) mixed layer N:P ratio and (F) Chlorophyll a (mg m^{-3}) concentration at the surface. Grey dots on NH_4^+ plot are data from 2016-2019, red dots are for data from 2015 and the black dots/black line shows the median trend of all these NH_4^+ data. Major tick marks represent the 1st of the month and minor tick marks represent 10th and 20th days.*

The water column was fully mixed at the WCO between 9th February and 7th April 2015. Stable stratifications occurred April 30th at which point the mean mixed layer depth (MLD) was 17 m (± 11 m). Stratification was broken down once during the bloom season on June 1st. Mixed layer nutrients reduced significantly during the spring/summer months, reflecting the typical seasonal pattern of phytoplankton growth and nutrient utilisation in these waters (Statham *et al.,* 2012). Mixed layer NO_3^- ranged from 0.01–85.6 mmol N m^{-2}, with minima and maxima measured on 7th June and 9th February, respectively (Figure 6). NO_3^- decreased to a low level (< 5 nmol N m^{-2}) on 27th April 2015 and remained low for the remainder of the campaign.

Surface layer NH_4^+ ranged from 0.5 - 36.8 mmol N m^{-2} and did not follow exactly the same trend as NO_3^- (Figure 6). Water column measurements of NH_4^+ during the 2015 campaign were inconsistently reported after the water column stratifies (Figure 6). To mitigate this uncertainty, a median seasonal trend for NH_4^+ concentrations was derived from all available WCO data from 2015 – 2019 (Figure 6). There are three distinct stages to the seasonal NH_4^+ concentration changes: (i) concentrations are low until mid-March because, unlike NO_3^- and PO_4^-, winter stocks are low; (ii) NH_4^+ concentrations increase almost three fold at the onset of the spring bloom and before stratification, with some inter-annual variation, indicating a biological turnover source of NH_4^+, e.g. NH_4^+ production due to grazing by zooplankton communities (Alcaraz, Saiz & Estrada, 1994); (iii) concentration decline to winter levels

297 after stratification, with occasional spikes, possibly due to secondary blooms or another point source
298 (e.g. river Tamar inputs).

299 Surface layer PO_4^{3-} ranged from 0.06 to 7.5 mmol P m^{-2}, with the minimum and maximum measured
300 on 30th June and February 9th 2015, respectively. The decline in PO_4^{3-} levels reflects the seasonal
301 nutrient depletion also observed in the dissolved inorganic nitrogen (DIN, = NO_3^-+ NH_4^+) levels (Figure
302 6). The majority of observed N:P ratios at the WCO L4 site were below the expected Redfield ratio (i.e.
303 < 16:1), meaning that PO_4^{3-} was predominately in excess (Figure 6). Excess PO_4^{3-} indicates that, with
304 sufficient light, addition of N to the system could stimulate greater biological productivity. Only when
305 there are elevated NH_4^+ concentrations in the water column does the N:P ratio rise above 16, which
306 could have led to P limitation within the phytoplankton community. P-limitation (or stress) at the WCO
307 has been measured previously following an influx of N-rich fresh water from the River Tamar, through
308 an increase in alkaline phosphatase activity (Rees *et al.,* 2009).

309 ## 4. DISCUSSION

310 The N dry deposition fluxes presented in this study are of a similar magnitude to measurements
311 elsewhere in western Europe during the past 20 years. Nitrogen (NO_3^- + NH_4^+) dry deposition flux at
312 PPAO ranged from 2.7 (± 1.1) to 620 (± 60) µmol N m^{-2} d^{-1}, which is similar to the range reported from
313 a coastal atmospheric station in De Haan, Belgium (7.86 – 405 µmol N m^{-2} d^{-1}; (Bencs *et al.*, 2009)).
314 The large N dry deposition event from 9th-23rd April 2015 was much higher than the fluxes observed
315 during the 1996/1997 sampling campaign at Mace Head, Ireland (9.3–203 µmol N m^{-2} d^{-1} (Spokes *et*
316 *al.*, 2000)). PPAO is closer than Mace Head to continental Europe, which may explain this difference.
317 Yeatman *et al*, (2001) collected aerosols from continental air masses at Weybourne (on the coast of
318 the North Sea, South East UK). The authors observed dry deposition fluxes between 166 and 1545
319 µmol N m^{-2} d^{-1}. Weybourne and the southern North Sea are very close (< 400 km) to the industrial
320 heartland of mainland Europe and thus more exposed than the PPAO/WCO to large N deposition
321 events. Other factors will have influenced the observations outlined above, including: (i) time that air

masses spend over industrial and agricultural regions; (ii) changing emission source strengths; (iii) different relative proportions of wet versus dry deposition; and (iv) different atmospheric chemical and physical processing.

Minimum NO_3^- and NH_4^+ concentrations were observed in North Atlantic Clean air masses. Maximum NO_3^- and NH_4^+ concentrations were observed when air came from Continental Europe (Figure 4). Interestingly, though NO_3^- and NH_4^+ emission sources are different, we observed that aerosol concentrations in Continental Europe samples co-varied and had a relatively constant 1:1 ratio (See Supplementary material). The aerosol concentration ratio may be determined by a similar average ratio in the emissions from the European continent. Indeed, estimated N emissions from continental European countries reported that annual average oxidised and reduced N emissions were also approximately 1:1 (Leip *et al.,* 2011). Several samples were noted to have back trajectories that traverse regions of high shipping density, which will contribute additional NO_3^- but not NH_4^+(Hertel *et al.*, 2012). In contrast with inorganic N fluxes, PO_4^{3-} dry deposition flux varied far less (one order of magnitude), most likely due to a more consistent local source in the form of mineral dusts and soils, rather than an integrated concentration over greater transport distances. Marine sources are not as significant: Baker *et al*., (2010) reported only 0.98– 4.89 nmol P m^{-2} d^{-1} dry phosphate fluxes in the middle of the North Atlantic Ocean (~3 orders of magnitude lower than this study). The significant difference is likely due to the proximity of PPAO to crustal source material and the association of PO_4^{3-} with coarse mode aerosols that have a much shorter atmospheric residence time (Duce *et al.*, 1991). PO_4 concentrations are low when polluted air masses came from Continental Europe, possibly because the low residence time of larger dust aerosols reduces the significance of non-arid source regions far from the sampling site. Furthermore, PO_4^{3-} airmass concentrations are typically low and it is challenging to accurately distinguish between the relative contribution of natural and anthropogenic sources to the low levels of aerosol PO_4^{3-} measured in this study.

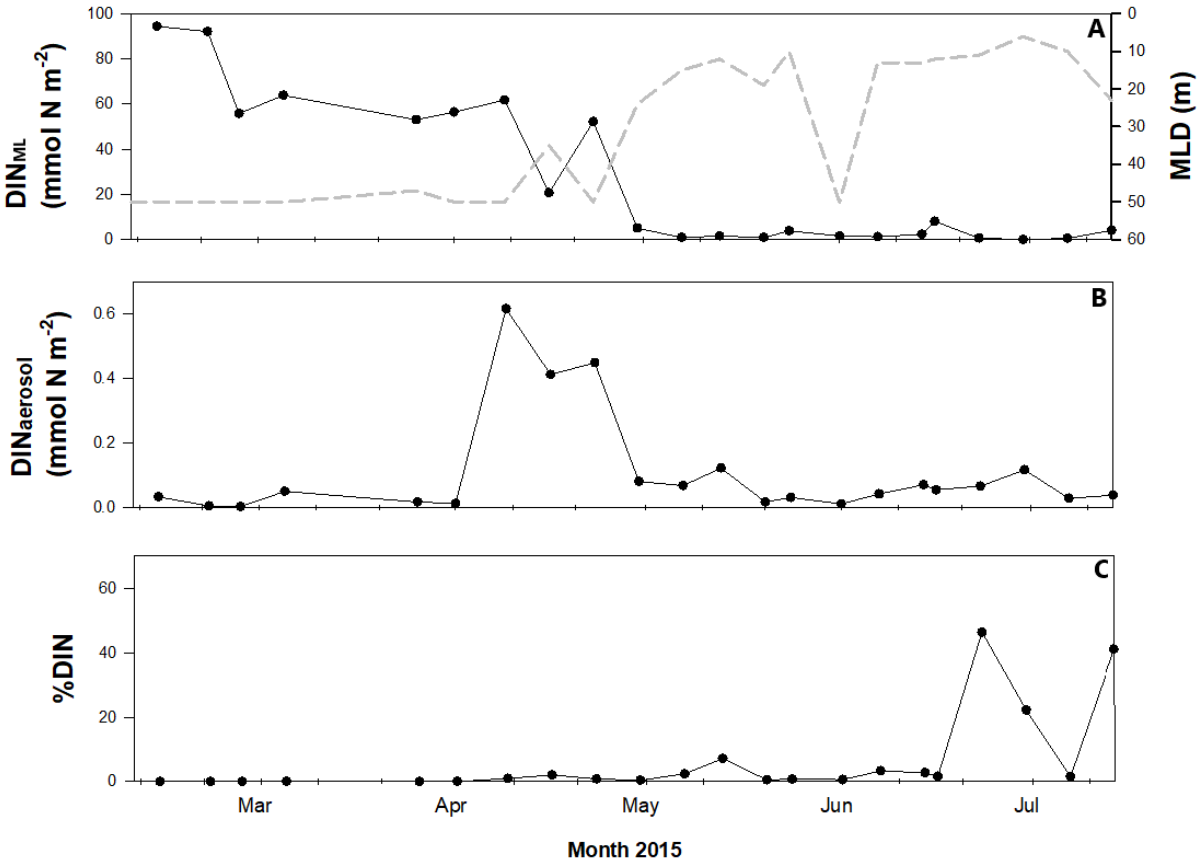
Impact of atmospheric aerosol deposition on surface mixed layer nutrients

Oceanic data from the WCO L4 marine time-series station and atmospheric data from the PPAO were used to assess the potential impact of aerosol nutrients on the local seawater (Figure. 7). As an indicator, a simple 1-D approach to compare the atmospheric aerosol N flux in one day ($DIN_{Aerosol}$) to the standing stock of DIN integrated to the base of the MLD/seabed (DIN_{ML}) as a percentage (*%DIN*):

$$\%DIN = 100 \times DIN_{Aerosol}/DIN_{ML} \quad (2)$$

This approach was initially applied to dry aerosol PO_4^{3-} deposition but the contributions were consistently below 0.1 %. Therefore, all further discussion of the response of the WCO L4 site to aerosol nutrient deposition and the potential biogeochemical consequences will focus on N deposition.

The water column was mixed down to the seabed prior to 13th April 2015, and DIN_{ML} levels were high (>10 mmol N m^{-2}) such that aerosol deposition had very little impact on seawater DIN (*%DIN* < 1 %, Figure 7). The onset of stratification around 1st May 2015 led to strong biological uptake and reduced DIN_{ML} levels to below 10 mmol N m^{-2}. The $DIN_{Aerosol}$ in early May was classified as Channel Mixed and this aerosol contributed up to 8% of DIN_{ML}. DIN_{ML} was almost completely depleted (< 10 mmol N m^{-2}) during June 2015 and after this time, deposition events resulted in %DIN exceeding 20% (Figure 7).



362

363 **Figure 7:** *Timeseries of: (A)Mixed layer dissolved inorganic nitrogen (DIN_{ML}), grey line is MLD used for*
364 *integration; (B) total aerosol dry nitrogen deposition flux ($DIN_{Aerosol}$); and (C) contribution of dry*
365 *deposition to water column inorganic N (%DIN, see text for how calculated). Major tick marks represent*
366 *the 1st of the month and minor tick marks represent 10th and 20th days.*

367 The deposition event on June 30th 2015 had the biggest potential impact and contributed almost 23 %
368 of DIN_{ML} at the WCO L4 station (Figure 7). Remarkably, %DIN was not significant during the very high
369 $DIN_{Aerosol}$ deposition events (Continental air masses) in April 2015 because the water was not yet
370 stratified and nutrient stocks were not depleted (Figure 7). Thus, sporadic atmospheric aerosol N
371 deposition can be significant source of nitrogen to shelf waters when DIN_{ML} is depleted during periods
372 of stratification and intense biological activity. Atmospheric circulation patterns are not tied to the
373 onset of stratification, however previous studies from PPAO have shown that winter dominance of
374 SW (marine) air masses is reduced in spring/summer allowing for more Continental air masses to occur

(Yang *et al.,* 2019; Yang *et al.*, 2016a; Yang *et al.*, 2016b). Had the high $DIN_{Aerosol}$ inputs occurred in May rather than in April, the *%DIN* would have been 14–37 %. Therefore, continental air masses have the potential to significantly influence the late spring and summer phytoplankton bloom at the WCO.

Another relative comparison can be made between aerosol deposition and vertical water column fluxes across the seasonal thermocline to the mixed layer. Summertime diffusive fluxes of NO_3^- across the stratified thermocline in the nearby Celtic Sea are 1.8 – 2 mmol NO_3^- m^{-2} d^{-1} (Birchill *et al*., 2017; Sharples *et al*., 2009). Hence the maximum dry deposition event observed at PPAO was equivalent to around a third of the typical daily diffusive flux across the thermocline.

Carbon fixation due to aerosol deposition into coastal waters

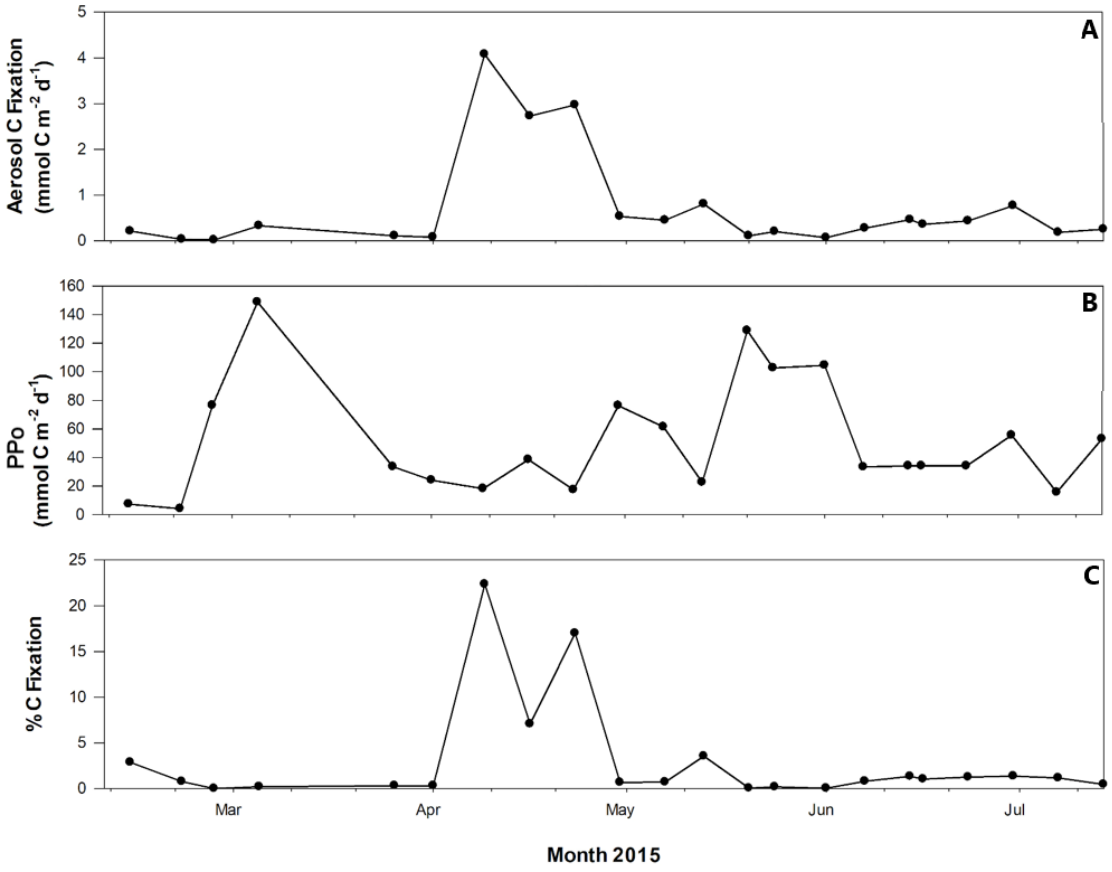
The assimilation of one mole of reactive nitrogen leads to 6.625 moles of carbon assimilation according to Redfield stoichiometry (106C : 16N : 1P; (Geider and La Roche, 2002; Redfield, 1958)). To calculate carbon fixation related to aerosol N deposition, we assume that all $DIN_{Aerosol}$ was bioavailable and that the other requirements for biological growth (other macro- and micro-nutrients, light, temperature) were met. The $DIN_{Aerosol}$ contribution of 0.02 – 0.62 mmol N m^{-2} d^{-1} during this study was potentially able to support 0.01 – 4.36 mmol C m^{-2} d^{-1} of carbon uptake (Figure 8A).

Previous studies have compared the potential carbon fixation due to $DIN_{Aerosol}$ to the seasonal average carbon fixation in the North Atlantic Ocean (Bencs et al., 2009, Spokes and Jickells, 2005). These studies observed that dry N deposition derived from continental European air masses could account for up to 15 % of the daily C fixation in the N E Atlantic Ocean (Bencs et al., 2009, Spokes and Jickells, 2005). Barnes *et al.,* (2015) report seasonal C-fixation rates and estimates for the WCO L4 station between 2003 and 2010. The average C- fixation rate during the season phytoplankton bloom at the WCO is 43.3 mmol C m^{-2} d^{-1} (Barnes *et al.,* 2015). We estimate C-fixation at the WCO L4 site (PP_o) using in situ chlorophyll observations (Barnes *et al*., 2014) (Figure 8B):

$$\alpha_{ph} = 0.0134 \times \text{Chl a} \times 0.0075 \quad (3)$$

399 $$PP_o = 0.0109 \times (\alpha_{ph} \times E_{par}) - 0.00018 \quad (4)$$

400 Where α_{ph} is absorption coefficient of phytoplankton, and E_{par} is photosynthetically active radiation.



401

402 **Figure 8:** *Timeseries of: (A) Carbon fixation due to $DIN_{Aerosol}$ input ($Cfix_{Aerosol}$), assuming uptake follows*
403 *the phytoplankton Redfield ratio; (B) Carbon fixation* (PP_o) *at the Western Channel Observatory L4*
404 *station estimated from in situ observations (see Eqn. 3); and (C) Proportion of PP_o at L4 that could be*
405 *supported by atmospheric N deposition, assuming all $DIN_{Aerosol}$ is bioavaliable (%Cfix = 100 x $Cfix_{Aerosol}$ /*
406 *PP_o). Major tick marks represent the 1st of the month and minor tick marks represent 10th and 20th*
407 *days.*

408 We compared C-fixation (PP_o) at the WCO with the C-fixation that could potentially be supported by
409 aerosol N deposition ($Cfix_{Aerosol}$) using $\%Cfix = 100 \times Cfix_{Aerosol}/PP_o$ (Figure 8C). The typical *%Cfix* was
410 ~1%. The *%Cfix* resulting from continental aerosol deposition during April was 15.5% on average, with

411 dry N deposition on April 9th potentially able to support a substantial amount of the mixed layer carbon
412 fixation (*%Cfix* = 22.4%).

413 Overall, these recent data highlight the continuation of high sporadic atmospheric nitrogen fluxes
414 originating from air circulation over highly populated land masses and the impact they can have on
415 surface ocean biogeochemistry. Spokes and Jickells, (2005) also reported significant wet and dry
416 nitrogen deposition (0.8 mmol m^{-2} d^{-1}) at Mace Head, Ireland, when air had been transported over the
417 European continent. Bencs *et al.,* (2009) reported a similar magnitude deposition event at De Haan,
418 Belgium. Both studies calculate that episodic deposition events containing polluted European aerosol
419 could support ~15 % of total surface water carbon fixation (Bencs et al., 2009, Spokes and Jickells,
420 2005). The magnitude of N deposition is a function of both location (proximity to aerosol N sources)
421 and prevailing wind direction. Neither of the events observed in Ireland or Belgium deposited as much
422 N as the PPAO event on April 9th 2015.

423 **Impact of N Deposition on Atlantic Shelf Waters**

424 In the previous sections the impact of dry N deposition to the coastal shelf waters near PPAO have
425 been evaluated and revealed two separate conclusions. While the carbon fixation estimates the
426 deposition events in April (corresponding to the highest atmospheric aerosol N concentrations) to
427 have the greatest impact, this was not the case when those deposition events were compared to the
428 standing nutrient stocks. From that investigation we conclude that N deposition has the most impact
429 once the nutrient stocks are depleted during the summer (June onwards) bloom season. Considered
430 together these calculations show that the impact of dry N deposition can have significance, but only
431 when certain conditions are met. However this also highlights the complexity of the cycling of
432 nutrients from the atmospheric into marine surface waters, and there are certainly other factors to
433 investigate in future work at this study site. For instance, the calculation we used to estimate the
434 contribution of $DIN_{Aerosol}$ to DIN_{ML} (Eqn. 2) assumes that DIN_{ML} is at steady state and does not consider
435 the potential importance of other N input and output terms due to uptake and removal processes.

Riverine input, atmospheric wet deposition, and diffusive fluxes of nitrogen across the thermocline may all influence DIN cycling in WCO waters.

Rainfall will play an important role for coastal and shelf N deposition during the seasons. For example, heavy rainfall over the River Tamar catchment has been shown to increase the freshwater flux of DIN into the English Channel, influencing the WCO L4 site. DIN concentrations at L4 after freshwater influx events in 2007 increased by 1.78 ± 0.20 µmol L^{-1}, coinciding with lowered salinity and increased P stress (Rees *et al.,* 2009).

Preliminary NO_3^- data in rainwater from PPAO show concentrations in the range of 5.6 - 49 µmol L^{-1}. Rainfall efficiently scavenges atmospheric aerosol such that wet N deposition is typically greater than dry N deposition and is likely to add a further significant seasonal flux to the shelf nitrogen budget. The studies in Ireland and Belgium measured twofold higher flux of wet deposition than dry deposition (Bencs *et al*., 2009, Spokes and Jickells, 2005). Thus, the total atmospheric N deposition in the WCO during our study would have been of higher magnitude if rainfall were considered, particularly as there were 9 major rain events at the PPAO during April 2015. Furthermore, organic N aerosol was not measured in this study, but reports from elsewhere suggest that it may represent 15 – 65 % of the total atmospheric N budget (e.g., Jickells *et al.*, 2013), so the effect of organic N deposition on marine biogeochemistry is likely to be even larger. Thus, the combined impact of dry plus wet N deposition and additional fluxes of organic nitrogen on shelf water biogeochemistry, clearly warrant further investigation.

5. Conclusions

This study investigated atmospheric aerosol N and P, their sources and the potential impact on surface water biogeochemistry at the WCO between February and July 2015. The highest concentrations of N in aerosol were linked to pollution sources in continental Europe. These aerosol samples contained significantly more N than samples from other source regions, and likely contribute substantial pulses of new N into surface waters at the WCO. These shelf waters were N-limited throughout the spring

bloom season, and severe N-depletion generally occurred after the onset of water column stratification in spring. Aerosol N deposition always exceeded aerosol P deposition (N:P ratio > 250 in polluted continental European air mass samples) and N:P was also greater than the typical seawater ratio (i.e., Redfield >16:1). Calculations demonstrate that aerosol-derived had the greatest impact on biological productivity in shelf waters once the water column became stratified and during sustained winds from mainland Europe, more than 20 % of water column carbon fixation can be supported by aerosol N deposition.

Acknowledgements:

This research was supported by a European Commission Marie Curie Career Integration Grant for S.J.U. (PCIG-GA-2012-333143 DISCOSAT), UK Natural Environment Research Council (NERC) (NE/K001779/1, NE/P021336/1) and a QR-funded University of Plymouth Scholarship. The contribution of T.G.B. and the WCO/PPAO are supported by funding from NERC specifically National Capability (Climate Linked Atlantic Sector Science, CLASS) for the WCO, ACSIS (The North Atlantic Climate System Integrated Study; NE/N018044/1) and ACRUISE (Atmospheric Composition and Radiative forcing changes due to UN International Ship Emissions regulations, NE/S005390/1) for PPAO. We are grateful to Trinity House (http://www.trinityhouse.co.uk/) for access and use of the Penlee building and to Mount Edgcumbe Estate (http://www.mountedgcumbe.gov.uk/) for providing access to the PPAO site. This is contribution no. 9 from the PPAO.

References

Alcaraz, M., Saiz, E. & Estrada, M. (1994) 'Excretion of ammonia by zooplankton and its potential contribution to nitrogen requirements for primary production in the Catalan Sea (NW Mediterranean)'. *Marine Biology*, 119 (1), pp. 69-76.

Baker, A. R. and Jickells, T. D. (2017) 'Atmospheric deposition of soluble trace elements along the Atlantic Meridional Transect (AMT)', *Progress in Oceanography,* 158, pp. 41-51.

Baker, A. R., Lesworth, T., Adams, C., Jickells, T. D. & Ganzeveld, L. (2010) 'Estimation of atmospheric nutrient inputs to the Atlantic Ocean from 50°N to 50°S based on large-scale field sampling: Fixed nitrogen and dry deposition of phosphorus'. *Global Biogeochemical Cycles*, 24 (3),

Baker, A. R., Weston, K., Kelly, S. D., Voss, M., Streu, P. & Cape, J. N. (2007) 'Dry and wet deposition of nutrients from the tropical Atlantic atmosphere: Links to primary productivity and nitrogen fixation'. *Deep Sea Research Part I: Oceanographic Research Papers*, 54 (10), pp. 1704-1720.

Baker, A. R., Jickells, T. D., Biswas, K. F., Weston, K. and French, M. (2006) 'Nutrients in atmospheric aerosol particles along the Atlantic Meridional Transect', *Deep Sea Research Part II: Topical Studies in Oceanography,* 53(14–16), pp. 1706-1719.

Barnes, M. K., Tilstone, G. H., Suggett, D. J., Widdicombe, C. E., Bruun, J., Martinez-Vicente, V. & Smyth, T. J. (2015) 'Temporal variability in total, micro- and nano-phytoplankton primary production at a coastal site in the Western English Channel'. *Progress in Oceanography*, 137 pp. 470-483.

Barnes, M. K., Tilstone, G. H., Smyth, T. J., Suggett, D. J., Astoreca, R., Lancelot, C. and Kromkamp, J. C. (2014) 'Absorption-based algorithm of primary production for total and size-fractionated phytoplankton in coastal waters', *Marine Ecology Progress Series,* 504, pp. 73-89.

509 Bencs, L., Krata, A., Horemans, B., Buczyńska, A. J., Dirtu, A. C., Godoi, A. F. L., Godoi, R. H. M.,
510 Potgieter-Vermaak, S. & Van Grieken, R. (2009) 'Atmospheric nitrogen fluxes at the Belgian coast:
511 2004–2006'. *Atmospheric Environment*, 43 (24), pp. 3786-3798.
512
513 Birchill, A. J., Clinton-Bailey, G., Hanz, R., Mawji, E., Cariou, T., White, C., Ussher, S. J., Worsfold, P. J.,
514 J, Achterberg, E., P and Mowlem, M. (2019) 'Realistic measurement uncertainties for marine
515 macronutrient measurements conducted using gas segmented flow and Lab-on-Chip
516 techniques', *Talanta,* 200, pp. 228-235.
517
518 Birchill, A. J., Milne, A., Woodward, E. M. S., Harris, C., Annett, A., Rusiecka, D., Achterberg, E. P.,
519 Gledhill, M., Ussher, S. J., Worsfold, P. J., Geibert, W. and Lohan, M. C. (2017) 'Seasonal iron depletion
520 in temperate shelf seas', *Geophysical Research Letters,* 44(17), pp. 8987-8996.
521
522 Björkman, K. M. & Karl, D. M. (2003) 'Bioavailability of dissolved organic phosphorus in the euphotic
523 zone at Station ALOHA, North Pacific Subtropical Gyre'. *Limnology and Oceanography*, 48 (3), pp.
524 1049-1057.
525
526 Chester, R. & Jickells, T. (2012) 'The Transport of Material to the Oceans: The Atmospheric Pathway',
527 *Marine Geochemistry.* John Wiley & Sons, Ltd, pp. 52-82.
528
529 Cornell, S. E. & Jickells, T. D. (1999) 'Water-soluble organic nitrogen in atmospheric aerosol: a
530 comparison of UV and persulfate oxidation methods'. *Atmospheric Environment*, 33 (5), pp. 833-840.
531
532 Duce, R. A., LaRoche, J., Altieri, K., Arrigo, K. R., Baker, A. R., Capone, D. G., Cornell, S., Dentener, F.,
533 Galloway, J., Ganeshram, R. S., Geider, R. J., Jickells, T., Kuypers, M. M., Langlois, R., Liss, P. S., Liu, S.
534 M., Middelburg, J. J., Moore, C. M., Nickovic, S., Oschlies, A., Pedersen, T., Prospero, J., Schlitzer, R.,

Seitzinger, S., Sorensen, L. L., Uematsu, M., Ulloa, O., Voss, M., Ward, B. & Zamora, L. (2008) 'Impacts of Atmospheric Anthropogenic Nitrogen on the Open Ocean'. *Science*, 320 (5878), pp. 893-897.

Duce, R. A., Liss, P. S., Merrill, J. T., Atlas, E. L., Buat-Menard, P., Hicks, B. B., Miller, J. M., Prospero, J. M., Arimoto, R., Church, T. M., Ellis, W., Galloway, J. N., Hansen, L., Jickells, T. D., Knap, A. H., Reinhardt, K. H., Schneider, B., Soudine, A., Tokos, J. J., Tsunogai, S., Wollast, R. & Zhou, M. (1991) 'The atmospheric input of trace species to the world ocean'. *Global Biogeochemical Cycles*, 5 (3), pp. 193-259.

Elser, J. J., Bracken, M. E. S., Cleland, E. E., Gruner, D. S., Harpole, W. S., Hillebrand, H., Ngai, J. T., Seabloom, E. W., Shurin, J. B. & Smith, J. E. (2007) 'Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems'. *Ecology Letters*, 10 (12), pp. 1135-1142.

Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B. & Cosby, B. J. (2003) 'The Nitrogen Cascade'. *Bioscience*, 53 (4), pp. 341-356.

Gardolinski, P. C. F. C., Hanrahan, G., Achterberg, E. P., Gledhill, M., Tappin, A. D., House, W. A. & Worsfold, P. J. (2001) 'Comparison of sample storage protocols for the determination of nutrients in natural waters'. *Water Research*, 35 (15), pp. 3670-3678.

Geider, R. & La Roche, J. (2002) 'Redfield revisited: variability of C:N:P in marine microalgae and its biochemical basis'. *European Journal of Phycology*, 37 (1), pp. 1-17.

Hansen, H. P. & Koroleff, F. (2007) 'Determination of nutrients', *Methods of Seawater Analysis.* Wiley-VCH Verlag GmbH, pp. 159-228.

561 Hertel, O., Skjøth, C. A., Reis, S., Bleeker, A., Harrison, R. M., Cape, J. N., Fowler, D., Skiba, U., Simpson,
562 D., Jickells, T., Kulmala, M., Gyldenkærne, S., Sørensen, L. L., Erisman, J. W. & Sutton, M. A. (2012)
563 'Governing processes for reactive nitrogen compounds in the European atmosphere'. *Biogeosciences*,
564 9 (12), pp. 4921-4954.
565
566 Holmes, R. M., Aminot, A., Kérouel, R., Hooker, B. A. & Peterson, B. J. (1999) 'A simple and precise
567 method for measuring ammonium in marine and freshwater ecosystems'. *Canadian Journal of*
568 *Fisheries and Aquatic Sciences*, 56 (10), pp. 1801-1808.
569
570 Jickells, T. D., Buitenhuis, E., Altieri, K., Baker, A. R., Capone, D., Duce, R. A., Dentener, F., Fennel, K.,
571 Kanakidou, M., LaRoche, J., Lee, K., Liss, P., Middelburg, J. J., Moore, J. K., Okin, G., Oschlies, A., Sarin,
572 M., Seitzinger, S., Sharples, J., Singh, A., Suntharalingam, P., Uematsu, M. & Zamora, L. M. (2017) 'A
573 reevaluation of the magnitude and impacts of anthropogenic atmospheric nitrogen inputs on the
574 ocean'. *Global Biogeochemical Cycles*, 31 (2), pp. 289-305.
575
576 Kim, T.-W., Lee, K., Duce, R. & Liss, P. (2014) 'Impact of atmospheric nitrogen deposition on
577 phytoplankton productivity in the South China Sea'. *Geophysical Research Letters*, 41 (9), pp. 3156-
578 3162.
579
580 Kocak, M. (2015) 'Solubility of Atmospheric Nutrients over the Eastern Mediterranean: Comparison
581 between Pure-Water and Sea-Water, Implications Regarding Marine Production', *Turkish Journal of*
582 *Fisheries and Aquatic Sciences,* 15, pp. 59-71.
583
584 Krishnamurthy, A., Moore, J. K., Mahowald, N., Luo, C., Doney, S. C., Lindsay, K. & Zender, C. S. (2009)
585 'Impacts of increasing anthropogenic soluble iron and nitrogen deposition on ocean biogeochemistry'.
586 *Global Biogeochemical Cycles*, 23 (3), pp. n/a-n/a.

Leip, A., Achermann, B., Billen, G., Bleeker, A., Bouwman, A. F., De Vries, W., Dragosits, U., Döring, U., Fernall, D., Geupel, M., Herolstab, J., Johnes, P., Le Gall, A. C., Monni, S., Nevečeřal, R., Orlandini, L., Prud'homme, M., Reuter, H. I., Simpson, D., Seufert, G., Spranger, T., Sutton, M. A., Van Aardenne, J., Voß, M. & Winiwarter, W. (2011) 'Integrating nitrogen fluxes at the European scale', in Sutton, M.A., Howard, C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., Van Grinsven, H. and Bruna, G. (eds.) *The European Nitrogen Assessment: Sources, Effects and Policy Perspectives.* Cambridge: Cambridge University Press.

Lentz, S., Shearman, K., Anderson, S., Plueddemann, A. and Edson, J., (2003) 'Evolution of stratification over the New England shelf during the Coastal Mixing and Optics study, August 1996–June 1997.' *Journal of Geophysical Research*, 108 (C1), pp. 1-14

Lesworth, T., Baker, A. R. & Jickells, T. (2010) 'Aerosol organic nitrogen over the remote Atlantic Ocean'. *Atmospheric Environment*, 44 (15), pp. 1887-1893.

Mackey, K. R. M., van Dijken, G. L., Mazloom, S., Erhardt, A. M., Ryan, J., Arrigo, K. R. and Paytan, A. (2010) 'Influence of atmospheric nutrients on primary productivity in a coastal upwelling region', *Global Biogeochemical Cycles,* 24(4).

Mahowald, N., Jickells, T. D., Baker, A. R., Artaxo, P., Benitez-Nelson, C. R., Bergametti, G., Bond, T. C., Chen, Y., Cohen, D. D., Herut, B., Kubilay, N., Losno, R., Luo, C., Maenhaut, W., McGee, K. A., Okin, G. S., Siefert, R. L. & Tsukuda, S. (2008) 'Global distribution of atmospheric phosphorus sources, concentrations and deposition rates, and anthropogenic impacts'. *Global Biogeochemical Cycles*, 22 (4), pp. n/a-n/a.

613 Maier, G., Glegg, G. A., Tappin, A. D., & Worsfold, P. J. (2012). A high resolution temporal study of
614 phytoplankton bloom dynamics in the eutrophic Taw Estuary (SW England). Science of The Total
615 Environment, 434, 228-239.
616
617 Martino, M., Hamilton, D., Baker, A. R., Jickells, T. D., Bromley, T., Nojiri, Y., Quack, B. & Boyd, P. W.
618 (2014) 'Western Pacific atmospheric nutrient deposition fluxes, their impact on surface ocean
619 productivity'. *Global Biogeochemical Cycles*, 28 (7), pp. 712-728.
620
621 Moore, C. M., Mills, M. M., Arrigo, K. R., Berman-Frank, I., Bopp, L., Boyd, P. W., Galbraith, E. D., Geider,
622 R. J., Guieu, C., Jaccard, S. L., Jickells, T. D., La Roche, J., Lenton, T. M., Mahowald, N. M., Maranon, E.,
623 Marinov, I., Moore, J. K., Nakatsuka, T., Oschlies, A., Saito, M. A., Thingstad, T. F., Tsuda, A. & Ulloa, O.
624 (2013) 'Processes and patterns of oceanic nutrient limitation'. *Nature Geosci*, 6 (9), pp. 701-710.
625
626 Myriokefalitakis, S., Nenes, A., Baker, A. R., Mihalopoulos, N. & Kanakidou, M. (2016) 'Bioavailable
627 atmospheric phosphorous supply to the global ocean: a 3-D global modeling study'. *Biogeosciences*,
628 13 (24), pp. 6519-6543.
629
630 Okin, G. S., Baker, A. R., Tegen, I., Mahowald, N. M., Dentener, F. J., Duce, R. A., Galloway, J. N., Hunter,
631 K., Kanakidou, M., Kubilay, N., Prospero, J. M., Sarin, M., Surapipith, V., Uematsu, M. & Zhu, T. (2011)
632 'Impacts of atmospheric nutrient deposition on marine productivity: Roles of nitrogen, phosphorus,
633 and iron'. *Global Biogeochemical Cycles*, 25 (2), pp. n/a-n/a.
634
635 Ottley, C. J. & Harrison, R. M. (1992) 'The spatial distribution and particle size of some inorganic
636 nitrogen, sulphur and chlorine species over the North Sea'. *Atmospheric Environment. Part A. General*
637 *Topics*, 26 (9), pp. 1689-1699.
638

639 Owens, N. J. P., Galloway, J. N. and Duce (1992) 'Episodic atmospheric nitrogen deposition to
640 oligotrophic oceans', *Nature,* 357(6377), pp. 397-399.
641
642 Park, G.-H., Lee, S.-E., Kim, Y.-i., Kim, D., Lee, K., Kang, J., Kim, Y.-H., Kim, H., Park, S. and Kim, T.-W.
643 (2019) 'Atmospheric deposition of anthropogenic inorganic nitrogen in airborne particles and
644 precipitation in the East Sea in the northwestern Pacific Ocean', *Science of The Total Environment,* 681,
645 pp. 400-412.
646
647 Redfield, A. C. (1958) 'THE BIOLOGICAL CONTROL OF CHEMICAL FACTORS IN THE ENVIRONMENT'.
648 *American Scientist*, 46 (3), pp. 230A-221.
649
650 Rees, A. P., Hope, S. B., Widdicombe, C. E., Dixon, J. L., Woodward, E. M. S. and Fitzsimons, M. F. (2009)
651 'Alkaline phosphatase activity in the western English Channel: Elevations induced by high summertime
652 rainfall', *Estuarine, Coastal and Shelf Science,* 81(4), pp. 569-574.
653
654 Schmidt, K., Birchill, A. J., Atkinson, A., Brewin, R. J. W., Clark, J. R., Hickman, A. E., Johns, D. G., Lohan,
655 M. C., Milne, A., Pardo, S., Polimene, L., Smyth, T. J., Tarran, G. A., Widdicombe, C. E., Woodward, E.
656 M. S., & Ussher, S. J. (2020). Increasing picocyanobacteria success in shelf waters contributes to long-
657 term food web degradation. Global Change Biology, 26(10), 5574-5587.
658
659 Sharples, J., Moore, C. M., Hickman, A. E., Holligan, P. M., Tweddle, J. F., Palmer, M. R. and Simpson,
660 J. H. (2009) 'Internal tidal mixing as a control on continental margin ecosystems', *Geophysical Research*
661 *Letters,* 36(23).
662

663 Singh, A., Gandhi, N. and Ramesh, R. (2012) 'Contribution of atmospheric nitrogen deposition to new
664 production in the nitrogen limited photic zone of the northern Indian Ocean', *Journal of Geophysical*
665 *Research: Oceans,* 117(C6).
666
667 Slinn, S. A. & Slinn, W. G. N. (1980) 'Predictions for particle deposition on natural waters'. *Atmospheric*
668 *Environment (1967)*, 14 (9), pp. 1013-1016.
669
670 Spokes, L. J. & Jickells, T. D. (2005) 'Is the atmosphere really an important source of reactive nitrogen
671 to coastal waters?'. *Continental Shelf Research*, 25 (16), pp. 2022-2035.
672
673 Spokes, L. J., Yeatman, S. G., Cornell, S. E. & Jickells, T. D. (2000) 'Nitrogen deposition to the eastern
674 Atlantic Ocean. The importance of south-easterly flow'. *Tellus B*, 52 (1), pp. 37-49.
675
676 Statham, P. J. (2012) 'Nutrients in estuaries — An overview and the potential impacts of climate
677 change'. *Science of The Total Environment*, 434 pp. 213-227.
678
679 Wang, Q., Song, J., Li, X., Yuan, H., Li, N., Duan, L. and Ren, C. (2019) 'Geochemical characteristics and
680 potential biogeochemical effect of water-soluble ions in atmospheric aerosols over the western
681 boundary regions of Pacific Ocean', *Atmospheric Research,* 227, pp. 101-111.
682
683 Woodward, E. M. S., Harris, C. (2019) 'Nutrient concentration profiles from long term time series at
684 Station L4 in the Western English Channel from 2000 to 2017'. *British Oceanographic Data Centre,*
685 *National Oceanography Centre, NERC, UK*. doi:10/c2rb.
686

687 Woodward, E. M. S. and Rees, A. P. (2001) 'Nutrient distributions in an anticyclonic eddy in the
688 northeast Atlantic Ocean, with reference to nanomolar ammonium concentrations', *Deep Sea*
689 *Research Part II: Topical Studies in Oceanography,* 48(4), pp. 775-793.
690
691 Yang, M., Bell, T. G., Brown, I. J., Fishwick, J. R., Kitidis, V., Nightingale, P. D., Rees, A. P. and Smyth, T.
692 J. (2019) 'Insights from year-long measurements of air–water CH4 and CO2 exchange in a coastal
693 environment', *Biogeosciences,* 16(5), pp. 961-978.
694
695 Yang, M., Bell, T. G., Hopkins, F. E., Kitidis, V., Cazenave, P. W., Nightingale, P. D., Yelland, M. J., Pascal,
696 R. W., Prytherch, J., Brooks, I. M. & Smyth, T. J. (2016a) 'Air–sea fluxes of CO2 and CH4 from the Penlee
697 Point Atmospheric Observatory on the south-west coast of the UK'. *Atmos. Chem. Phys.*, 16 (9), pp.
698 5745-5761.
699
700 Yang, M., Bell, T. G., Hopkins, F. E. & Smyth, T. J. (2016b) 'Attribution of atmospheric sulfur dioxide
701 over the English Channel to dimethyl sulfide and changing ship emissions'. *Atmos. Chem. Phys.*, 16 (8),
702 pp. 4771-4783.
703
704 Yeatman, S. G., Spokes, L. J., Dennis, P. F. & Jickells, T. D. (2001) 'Can the study of nitrogen isotopic
705 composition in size-segregated aerosol nitrate and ammonium be used to investigate atmospheric
706 processing mechanisms?'. *Atmospheric Environment*, 35 (7), pp. 1337-1345.
707
708 Yeatman, S. G., Spokes, L. J. & Jickells, T. D. (2001) 'Comparisons of coarse-mode aerosol nitrate and
709 ammonium at two polluted coastal sites'. *Atmospheric Environment*, 35 (7), pp. 1321-1335.
710
711