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Marine Matters

Pelagic N-cycling during the UK-OA cruise D366 Darren Clark

To make measurements of N-cycle parameters;

- 1. In the surface ocean at stations around the UK
- 2. During OA array's







Overview of the pelagic N-cycle



CTD casts at 11 stations in UK shelf seas. Samples taken at 55% sPAR.

Parameter	Status
$\rm NH_4^+$ assimilation (3 hour incubations)	Data available
NO_2^- assimilation (3 hour incubations)	Data available
NO_3^- assimilation (3 hour incubations)	Data available
[PON]	Data available
$\rm NH_4^+$ regeneration	Data available
NH ₄ ⁺ oxidation	Data available
NO_2^- oxidation	Data available

OA arrays.

Parameter	Status
NH_4^+ assimilation (24 hour incubations)	Sample analysis underway
NO ₂ ⁻ assimilation (24 hour incubations)	Sample analysis underway
NO ₃ - assimilation (24 hour incubations)	Sample analysis underway
[PON]	PON analysis underway
NH_4^+ regeneration	Data available
NH ₄ ⁺ oxidation	Data available



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Comparison between N-cycle parameter values measured at 55% sPAR (\approx 5-15m) by GC/MS & IRMS methods (average in brackets).

Parameter	N/S. Atlantic gyres	µ-layer	SOLAS-ICON	UKOA stations		
NH_4^+ (µmnol l ⁻¹)	0.004 - 0.102	0.019 - 0.138	0.06 - 1.27	0.120 - 0.818		
NO ₂ -	0.001 - 0.052	0.001- 0.054	0.27 - 0.71	0.007 - 0.052		
NO ₃ -	0.001 - 0.187	0.001 - 0.714	4.52 - 12.75	0.042 - 0.953		
PON (µmol l ⁻¹)	n.d	0.55 - 1.30	0.80 - 3.38	1.02 - 1.63		
DIN assimilation (nmol l ⁻¹ h ⁻¹)						
ρNH ₄ ⁺	n.d	0.98 - 12.09 (6.1)	6.1 - 71.7 (24.6)	1.79 - 40.06 (17.46)		
ρNO ₂ -	n.d.	n.d.	n.d.	0.01 - 1.59 (0.61)		
ρNO ₃ -	n.d.	0.11 - 3.74 (0.7)	2.0 - 65.7 (18.2)	0.42 - 9.03 (3.99)		
DIN regeneration rate (nmol l ⁻¹ h ⁻¹)						
$\rm NH_4^+$ regeneration	0.38 - 3.31 (1.5)	0.09 - 2.52 (0.90)	9.02 - 143.32 (46.3)	3.50 - 14.6 (7.67)		
$\rm NH_4^+$ oxidation	0.03 - 0.40 (0.1)	0.03 - 3.74 (0.58)	0.30 - 9.71 (4.2)	0.01 - 1.85 (0.74)		
NO_2^- oxidation	0.04 - 1.28 (0.5)	0.03 - 24.76 (2.24)	2.93 - 81.11 (31.8)	0.05 - 28.9 7 (6.15)		



- DIN pool generally dominated by regenerated N (NH_4^+) in surface waters (55% sPAR) around UK.
- [PON] values at individual stations exceeded those measured in the Iberian upwelling.
- Contribution to cell-N dominated by NH_4^+ assimilation at all stations.

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NO₂⁻ assimilation rarely measured - contributed ≈ 5% to cell-N assimilation at individual stations (generally < 2%).







• N-regeneration measured in the surface ocean at stations around the UK.

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- At many stations a substantial fraction of the DIN pool turned over within a day, exceeding 1 d⁻¹ in the SW.
- The 'whole pool' turnover resembles that of the open ocean and contrasts with that of upwelling regions.





- This study aimed to investigate how OA conditions influenced NH_4^+ regeneration and nitrification.
- Previous OA related studies of NH₄⁺ oxidation have all found that rates drop under OA conditions (NH₄⁺↔NH₃). However, studies have been conducted in a range of matrices including soil/sludge/sediment/seawater.

Study	Location & depths	Method	Comment
Huesemann et al 2002	Washington (Coastal Pacific). Samples from 0.5m and 160 m (photic and aphotic depths)	Metabolic inhibitors	 i) NH₄⁺ addition possibly 1000 times greater than ambient – substantial perturbation to the system. ii) Stimulation of NH₄⁺ oxidation activity/potential rates measured?
Berman et al 2010	HOT/BATS/ALOHA. Samples from 45, 175, 240m (aphotic depths only)	¹⁵ N methods with trace additions	i) Strong evidence for drop in NH_4^+ oxidation rates from aphotic samples.

- This study may represent the first investigation of N-regeneration within the photic zone using trace additions of ¹⁵N.
- Competition for NH_4^+ between phytoplankton and NH_4^+ oxidising organisms will be an important factor in the photic zone.
- How is the bacterial degradation of organic matter influenced by OA?
- A significant fraction of regenerated N enters the nitrification pathway is this modified under OA conditions?



Fraction of NH₄⁺ entering NH₄⁺ oxidation pathway

- 0.04-0.45 NW African upwelling
- 0.01-0.43 Iberian Peninsula
- 0.21-0.33 Monterey Bay (Ward 2005)
- 0.05-0.33 Monterey bay (Wankel et al 2007)
- 0.00-0.09 UK shelf seas
- ??? UK shelf sea under OA conditions





• Evident variability in rates and trends for both NH₄⁺ regeneration and NH₄⁺ oxidation





- Average rates for treatments highlight potential structure; sources of variability will include geographical location further analysis may draw out significant trends.
- For NH_4^+ regeneration:
 - Results imply an increase in regeneration rates above the average measured for UK waters.
 - If this is found to be robust, results imply increased bacterial degradation of DOM pool and associated CO₂ release.
 - DIN pool concentration may increase, shifted further towards NH₄⁺. Changes in phytoplankton community structure and productivity may be anticipated.
- For NH_4^+ oxidation:
 - No convincing trend. Nitrifying bacteria/archaea represent a small, slow growing fraction of the total population.
 - The fraction of NH_4^+ entering the nitrification pathway is yet to be determined requires OA NH_4^+ assimilation data.



Conclusions

- Relatively active N –cycling takes place within the photic zone of the 'present day' UK shelf seas.
- Bacterial degradation of DOM and regeneration of NH_4^+ increased above UK average under OA conditions.
- The influence of OA upon nitrification is less clear.

Next steps

• Complete sample analysis to allow comprehensive data analysis to be undertaken.

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