Plymouth Marine Laboratory: Core cruise 2004 Phosphate & Iron Addition Experiment (*FeeP*)

CD156

RRS Darwin 24th April – 24th May 2004 Santa Cruz de Tenerife – Santa Cruz de Tenerife

Chief Scientist : Prof. N.J.P. Owens

(Compiled by Dr. P.D. Nightingale)





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We would like to thank all those involved with this experiment from conception through to delivery. This was a huge effort both by those on board the Charles Darwin and those lucky souls on the RV Poseidon (who were also allowed the luxury of a swim call). We would also like to thank those back at home who helped this cruise take place including Ian Joint, Peter Miller, Chris Wing and the PML directorate team. The officers, engineers and crews of both ships were fantastic in their delivery of what was at times a testing operation.



BACKGROUND

Between the 24th April and 26th May 2004 Plymouth Marine Laboratory in collaboration with scientists from NIWA, New Zealand, Laboratoire Arago, France and University of East Anglia conducted a two-ship exercise using RRS Charles Darwin and RV Poseidon to test the following hypothesis:

'The supply of, and the interaction between, iron and phosphorous control biological activity and fluxes in the subtropical North Atlantic.'

An experimental area in international waters to the west of the Canary Islands was selected following an intense period of vertical and horizontal mapping by the Charles Darwin. Using SF_6 as a tracer for amended waters, two separate experiments were performed. The first (5th – 15th May) involved the addition of 20 tonnes of anhydrous monosodium phosphate at 10 m depth over an area of approximately 25 km2, centered at 27.8°N 23.3°. The second experiment was conducted following a mid-cruise return by the Poseidon to Tenerife between 16th and 22nd May, at 27.5°N 22.5°W when 5 tonnes of acidified iron sulphate were added over the first 12 hours and, following a 15 hour recovery period, 20 tonnes of phosphate were added on the top of the original iron/SF₆ patch. Measurements of nutrient cycling, biogenic gases, and biological activity were monitored prior to and after deployment (IN stations) of the fertilised patches relative to several (OUT) control stations.



SCIENTIFIC PERSONNEL

Prof. Nick Owens	PML	Principal scientist & UOR
Dr. Steve Archer	PML	DMS/DMSP
Tim Fileman	PML	Underway SF ₆ & patch release
James Fishwick	PML	Optics & UOR
Dr. Laura Goldson	PML	Iodocarbons
Carolyn Harris	PML	Nutrient analysis
Dr. Susan Kimmance	PML	Viral & grazing impacts
Malcolm Liddicoat	PML	Methyl bromide
Alex de Menezes	PML	Pigments
Dr. Philip Nightingale	PML	Underway & vertical SF6 analysis
Dr. Mireille Pujo-Pay	LA	Organic phosphate and nitrate
Dr. P. Conan	LA	Organic phosphate and nitrate
Dr. Glen Tarran	PML	Flow cytometry
Dr. Ricardo Torres	PML	Physics
Dr. Simon Usher	UoP	Iron chemistry
Malcolm Woodward	PML	Nutrient Analysis

PML = Plymouth Marine Laboratory, West Hoe, Plymouth, PL1 3DH, UK

LA = Laboratoire Arago, BP44, 666512, Banyuls sur Mer, France

UoP = University of Plymouth, Drake Circus, Plymouth, PL4 8AA

DIARY OF EVENTS

(Based on the Master's [Peter Serjeant] report) All times in text are UTC (V/l keeping UTC+1 at departure; UTC from 0100/27th April; UTC+1 from 0300/23rd May)

2004-04-24

- Forenoon: Scientists & OED technicians join vessel & continue mobilisation (on-going from 2004-04-21).
- 1200 Scientists & Technicians signed-on & given full Safety Briefing followed by Safety & Familiarisation tour of vessel.

2004-04-25

	Mobilisation continues. ETD 1300hrs
1215	Sailing postponed to 0930/26th at request of Principal Scientist. Set-up
	continues in Main Lab.

1500-1700 P. Nightingale (Scientist) to hospital.

2004-04-26

0730	PS reports Scientific Party ready for sailing.
0840	Steering gear checks completed
0900	All Bridge equipment tested & satis. ME to Bridge Control and tested ahead & astern. BT tested.
0915	All pre-sailing checklists received & satisfactory. All persons on board & visitors ashore.
0930	PoB Jonento; RSBE
0940	Last line
0955	Pilot away; v/l clearing breakwaters
1000	FAOP; N. Breakwater brng 339 x 0.75nm
1109	28 16.8N 16 18.7W Increase offing prior to CTD trial
1358	27 54.5N 16 32.0W Hove-to & CTD deployed
1453	CTD recovered to deck; v/l resuming passage
1515	Emergency & Boat musters + associated familiarisation exercises
1718	27 53.6N 16 56.3W Commence Chernikeef log calibration runs
1924	Complete calibration & resume W-bound passage
2300	27 58.0N 17 38.2W

2004-04-27

[Ship's clocks retarded 1 hr at 0100 UTC]

L. L	
0600	27 57.7N 19 04.2W
0936	27 58.1N 19 45.3W Temporary heave-to to deploy PES & TMS 'fish'
1032	27 58.3N 19 45.9W Commence trial wire & UOR deployments
1250	27 58.6N 20 07.3W Recovery of UOR & PES
1300	Resume passage towards 'mapping' zone
1413	27 58.6N 20 21.1W Reduce to 2 knots for conveyor & mixing tanks trial
1500	Resume passage
2334	27 58.0N 22 00.0W Hove-to @ Station IM0

2004-04-28

0007	CTD deployed & veering to 500m
0042	27 58.1N 22 00.2W CTD recovered
0113	27 57.8N 22 00.4W Comm UOR deployment
0120	Towing UOR towards next station
0630	97 91 ON 99 11 AW LIOD recovered

0630 27 21.9N 22 41.4W UOR recovered

0703	27 21.7N 22 41.6W CTD deployed @ Station IM1
0703	27.21 ON 22.42 1W Comm LOD deployment
0809	27 21.9N 22 42.1W Comm UOR deployment
U020 1991	10Wing UOK towards next station
1331	27 57.01 23 20.2W UUK recovered
1408	27 57.9N 23 26.4W CTD deployed @ Station IM2
1502	CID recovered
1521	Secure on deck; deviation to search for NIOZ mooring
1727	2758.0 N 2348.2 W On location
1734	Argos Buoy sighted
1810	27 58.6N 23 48.8W Pick up line grappied
1840	Recovery in progress via Stod gantry & Core winch
1850	Ist current meter removed
1855	Bare-end of wire recovered; preparations for CTD deployment
1936	27 58.2N 23 49.0W CTD deployed @ Station IMINIOZ
2006	CID recovered
2018	27 58.01 23 48.8W Deploying UOR on passage to next station
2004-04-29	
0343	26 45.7N 23 28.0W UOR recovered
0359	26 45.3N 23 28.1W CTD deployed @ Station IM3
0500	CTD recovered
0520	26 44.7N 23 27.9W Deploying UOR on passage to next station
0921	26 43.0N 22 40.1W UOR recovered
0932	TMS recovered
1004	26 42.8N 22 44.1W CTD deployed @ Station IM4
1114	CTD recovered; v/l remains hove-to for results assessment
1315	26 42.9N 22 43.6W Deploying UOR on passage to next station
1818	26 08.1N 23 23.8W UOR recovered; TMS redeployed
1838	26 08.2N 23 23.8W CTD deployed @ Station IM5
1931	CTD recovered
1942	26 08.6N 23 23.6W Deploying UOR on passage to next station
2004-04-30	
0020	25 36.5N 23 58.4W UOR recovered
0047	25 35.9N 23 58.6W CTD deployed @ Station IM6
0124	CTD recovered
0134	25 35.5N 23 58.6W Deploying UOR on passage to next station
0814	24 49.4N 24 49.6W UOR recovered
0846	24 49.3N 24 49.5W CTD deployed @ Station IM7
0945	CTD recovered
1000	V/l remains hove-to for results assessment
1350	24 46.8N 24 49.6W Set co. 357 degs towards next station
1430	24 53.6N 24 50.2W Deploying UOR
1615	Emergency muster & exercises
<u>2004-05-01</u>	
0422	27 09.8N 25 01.5W UOR recovered
0441	27 09.7N 25 01.8W CTD deployed @ Station IM8
0503	CTD recovered
0511	27 09.6N 25 01.8W Deploying UOR on passage to next station
0930	27 48.4N 25 01.6W UOR recovered
1000	

1048	CTD recovered; v/l remains hove-to for results assessment
1221	27 48.1N 24 58.9W Deploying UOR on passage to next station
1730	28 25.2N 24 22.6W UOR recovered
1757	28 25.1N 24 22.4W CTD deployed @ Station IM10
1848	CTD recovered
1900	28 25.3N 24 22.9W Deploying UOR on passage to next station
2342	28 38.4N 23 37.4W UOR recovered
2355	28 38.3N 23 37.3W CTD deployed @ Station IM11
2004-05-02	
0020	CTD recovered
0028	28 38 0N 23 37 2W Deploying UOR on passage to next station
0520	2751.6N 23 30.4W UOR recovered: v/l 'dodging' in vicinity: rendezvous with
0020	'Poseidon'
0824	27 54.3N 23 30.8W CTD deployed @ Station IM12
0926	CTD recovered: processing samples & preparing for boat transfer
1020	27 54.5N 23 30.5W V/l lving a-hull: RIB swung to stbd bulwarks
1030	RIB away to 'Poseidon' – six persons aboard
1035	Four scientists safely transferred to 'Poseidon'
1039	RIB recovered to stbd bulwarks
1200	27 54.0N 23 30.5W V/l remains hove-to
1300	27 53.2N 23 30.3W 'Poseidon' approaching for second transfer
1315	'Charles Darwin' RIB away – four persons & gear aboard
1350	27 52.5N 23 30.0W Two return trips completed – three 'CD' scientists remain
	aboard 'P' RIB recovered to bulwarks
1400	27 52.5N 23 29.7W V/l hove-to, head-to-wind, awaiting instructions. RIB
	transferred to cradle
1550	V/l repositioning to station for start of CTD grid survey
1614	27 50.6N 23 29.7W CTD deployed @ Station IM13
1640	CTD recovered; v/l transiting to next station
1718	27 53.5N 23 26.1W CTD deployed @ Station IM14
1745	CTD recovered; 'Poseidon preparing for boat transfer
1815	27 53.4N 23 25.8W 'CD' lying a-hull; 'Poseidon' inflatable in transit
1825	27 53.2N 23 25.8W Three scientists re-embarked & gear loaded; 'P' inflatable
	clear.
1910	27 57.1N 23 21.9W Streaming & testing patch deployment gear
2046	27 58.5N 23 19.9W Testing completed
2100	27 58.4N 23 19.9W CTD deployed N. of Station IM15
2130	CTD recovered; transiting to next station
2223	27 53.6N 23 18.0W CTD deployed @ IM16
2250	C1D recovered; V/1 in transit
2342	27 50.2N 23 21.9W C1D deployed @ IM17
<u>2004-05-03</u>	
0009	CTD recovered; v/l in transit
0100	27 46.6N 23 26.0W CTD deployed @ IM18
0126	CTD recovered; v/l in transit
0210	27 43.1N 23 22.0W CTD deployed @ IM19
0235	CTD recovered; v/l in transit
0328	27 46.7N 23 17.9W CTD deployed @ IM20
0355	CTD recovered; v/l in transit
0445	27 50.0N 23 14.1W CTD deployed @ IM21

0516 CTD recovered; v/l in transit

	0602	27 46.6N	23 10.2W	CTD deployed @ IM2	22
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- 0630 CTD recovered; v/l in transit
- 27 43.1N 23 14.2W CTD deployed @ IM23 0712
- CTD recovered; v/l in transit 0740
- 27 39.5N 23 18.1W CTD deployed @ IM24 0821
- CTD recovered; v/l transiting to centre of grid 0847
- 27 48.5N 23 20.0W CTD deployed @ IM25 1018
- 1104 CTD recovered; v/l awaiting PS instructions
- 1305 27 50.9N 23 20.2W Drifter buoy deployed
- Commence trial expanding square track around beacon 1310
- 1445 27 51.2N 23 20.3W Drifter recovered
- 27 50.0N 23 29.8W Deploying UOR @ commencement of repeat grid survey 1547
- 27 57.2N 23 22.0W Passing through IM15 1650
- 27 39.5N 23 18.0W Passing through IM24 @ completion of grid survey (UOR) 2110
- 2130 UOR recovered; v/l 'dodging' overnight

2004-05-04

0800	27 48.5N 23 19.9W Hove-to at central position
0842	27 48.8N 23 19.8W CTD deployed @ Station T0 IN
1004	CTD recovered; v/l awaiting PS instructions
1248	27 50.4N 23 19.4W TMS recovered; preparations for patch deployment
1414	Commence mixing phosphate in deck tanks
1528	27 48.7N 23 20.0W Drifter Buoy marker deployed
1556	27 48.7N 23 20.3W Depressor weight & pumping tube deployed over stern to
	10m
1610	Commence pumping to bring mix up to saturation
1906	27 49.0N 23 19.7W Commence expanding square patch deployment from
	Drifter V/l @ 2 knots thro' water throughout deployment N/S & E/W tracks @
	500m spacings from centre
2004-05-05	
0845	27 47.8N 23 20.0W Complete first circuit of expanding square @ WPT 22
0945	27 46.6N 23 18.8W Back at Drifter & recommencing expanding square
1636	27 47.7N 23 17.6W Complete patch deployment; v/l 'dodging' clear of patch
1906	27 47.2N 23 18.7W V/l hove-to near Drifter
1912	27 47.2N 23 18.7W CTD deployed @ T1 IN
2013	27 47.3N 23 18.4W CTD recovered; TMS deployed; v/l 'dodging' - awaiting
	scientific instructions
2400	27 46.2N 23 17.5W V/l remains hove-to
2004-05-06	
0100	27 46.6N 23 17.3W Commence 'bow-tie' non-toxic survey
0352	27 46.1N 23 16.8W Complete 'bow-tie' survey; v/l hove-to vicinity Drifter
	buoy
0400	27 JG ON 22 16 OW CTD deployed @ T2 IN

- 27 46.0N 23 16.9W CTD deployed @ T2 IN 0408 CTD recovered; v/l remains in vicinity
- 0436
- 27 45.4N 23 16.9W CTD deployed @ T3 IN 0715 CTD recovered; v/l remains in vicinity
- 0818
- 1036 27 45.2N 23 16.2W Sampling sensor streamed
- 1117 27 45.5N 23 16.3W Sensor recovered
- 27 44.8N 23 17.1W CTD deployed @ Station T4 IN 1235
- CTD recovered; comm. optic dips over stern 1311
- Optic line recovered; v/l remains in vicinity 1342

1758 2245	27 44.9N 23 17.2W Commence non-toxic sampling transects around patch 27 45.8N 23 15.0W Transects continue
2004 05 07	
$\frac{2004-03-07}{0195}$	27 20 2N 22 17 2W Temperany beause to @ scientific request
0123	27 39.51 25 17.2 W Temporary neave-to @ scientific request 27 20 5N 22 17 2W Decume compling transacts
0208	27 59.51N 25 17.2 W Resume sampling transects
0721	27 43.11N 23 12.7 W Complete transects; closing C1D station
0743	27 43.31N 23 13.2W CTD deployed @ 13 IN
0045	CTD recovered; awalting scientific instructions
1200	27 42.2N 23 12.2W Optics rig deployed
1245	27 44.01 23 12.9W Optics rig recovered
1329	27 44.01 23 13.3W CID deployed @ 16 IN
1415	CTD recovered – sampling & securing
1443	In transit to out-of-patch station
1550	27 44.2N 23 20.9W CTD deployed @ 17 OUT
1615	Safety drills (Boats swung; I raft familiarisation; PS & SR DVD)
1648	CID recovered
1700	V/I bound towards Poseidon for boat transfer
1750	27 44.7N 23 14.6W Temporarily hove-to for safe deployment check
1832	27 45.7N 23 15.8W Hove-to & RIB released – two crew on board
1841	27 45.6N 23 15.9W RIB returned with gear & recovered to foc sie deck for
1000	disembarkation
1900	RIB stowed; V/I bound 5 N of Drifter for food waste disposal
1948	27 47.51N 23 14.4W V/I bound for central position
2030	27 41.7N 23 18.6W Hove-to vicinity of Drifter, awaiting instructions
2122 2251	27 41.01 25 15.7 W Commence expanding square non-toxic survey from Drifter
2334	27 40.51V 25 15.0VV Survey continues
<u>2004-05-08</u>	
0700	27 45.1N 23 15.3W Break off from exp. square; sampling courses to scientific
	requirements
1000	27 40.9N 23 14.5W Cease survey & manoeuvring to NE of Drifter
1110	27 41.0N 23 14.2W CTD deployed @ Station T8 IN
1216	CTD recovered
1244	27 41.0N 23 14.2W Optics rig deployed
1305	Optics rig recovered; v/l steaming clear of patch
1452	27 41.3N 23 02.8W Optics rig deployed
1519	Optics rig recovered
1550	27 41.5N 23 02.9W CTD deployed @ Station T9 OUT
1640	CTD recovered
1726	Set co. for Drifter
1852	27 38.9N 23 16.4W Hove-to close S. of Drifter; sci. preparations for replacement
1940	27 39.21N 23 16.43W Drifter grappled to deck (Drogue & thermistor string outboard)
1952	27 39.19N 23 16.46W Drifter re-streamed with replacement transmitter
2012	27 39.4N 23 16.5W Deploying UOR @ commencement of mapping survey
<u>2004</u> -05-09	
0256	27 38.5N 23 19.0W Complete N/S transects to E & W of Drifter
0352	27 40.7N 23 16.3W UOR recovered; v/l repositioning
0435	27 39.6N 23 15.5W CTD deployed @ Station T10 IN

- 0450 CTD recovered
- 0518 27 39.6N 23 15.5W Commence non-toxic 'Spiral' survey @ 5-6 knots from patch

0719	Survey completed
0733	27 41.5N 23 13.8W CTD deployed @ Station T11 IN
0841	CTD recovered; scientific assessment
1118	27 41.9N 23 13.9W Optic rig deployed
1200	Optic measurements completed
1242	27 42.3N 23 13.5W CTD deployed @ Station T12 IN
1318	CTD recovered: processing, securing & retiring from patch
1520	27 47 5N 23 13 8W CTD deployed @ Station T13 OUT
1617	CTD recovered
1708	27.48 ON 23.14 AW LIOR deployed for overnight mapping run
1800	27 42 6N 23 15 2W Hove to for TMS recovery (fault): thence resume track
2250	27 42.01 23 13.2 W TIOVE-to for TWS recovery (lault), thence resume track
2330	27 SO.ON 25 02.1 W CORTUNCONTINUES
9004 05 10	
<u>2004-05-10</u>	97 40 CNI 99 07 CNI Managing and stated LIOD managed back of CTD
0621	27 42.6N 23 07.6W Mapping run completed; UOR recovered; set co. for CTD
0707	
0/3/	27 39.5N 23 13.2W CTD deployed @ Station 114 IN
0841	CID recovered
0945 – 1045	Vicinity 27 40.0N 23 13.5W Boat transfers using 'CD' RIB; 2 persons to
1050	Poseidon'; I to CD'.
1052	27 39.3N 23 13.9W TMS deployed
1109	Optics rig measurements
1132	27 39.8N 23 13.8W Optics measurements completed
1225	27 40.2N 23 13.9W CTD deployed @ Station T15 IN
1302	CTD recovered; processing then v/l heading to verify buoy position
1330	Safety briefing completed for newly boarded Scientist
1358	27 37.4N 23 20.5W Drifter sighted; v/l south-bound clear of patch
1458	27 33.1N 23 20.7W CTD deployed @ Station T16 OUT
1558	CTD recovered; processing then v/l repositioning to buoy
1715	27 37.3N 23 21.0W Hove-to @ Drifter ('D')
1825	TMS recovered; v/l repositioning 2nm NE
1954	27 39.5N 23 19.9W Drifter 'C' deployed
2035	27 37.9N 23 22.0W Drifter 'D' grappled & recovered
2115	27 39.5N 23 20.8W V/l hove-to off Drifter 'C'
2230	Repositioning upwind of Drifter 'C'
2337	29.39.5N 23.20.1W Drifter 'D' redeployed with full thermistor string
2001	Commence 'box-section' ADCP survey @ 4 knots
2004-05-11	
0600	27 39.9N 23 21.3W Complete ADCP survey & hove-to @ Drifter 'D'
0608	As above CTD deployed @ Station T17 IN
0656	CTD recovered: v/l repositioning for sequential CTDs
0806	27 42 7N 23 18 3W CTD deployed @ Station T18 IN
0851	CTD recovered
1006	27 41 5N 23 10 7W/ CTD deployed @ Station T10 IN
1056	CTD recovered
11/6	27 10 5N 23 20 1W Ontice rig stroomed vicinity Drifter 'D'
1140	Optics rig recovered
1200	27 10 7N 22 20 2W CTD daplayed @ Station T20 IN
1611	CTD recovered
1200	UID recovered
1410	CTD reserves de se (1 remonitération : Composition : Compo
1400 1007	27 40 9NL 99 99 1W. Differ recovered and state still and for the second state of the s

1635	27 39.2N 23 22.3W CTD deployed @ Station T22 IN
1645	Deployment aborted due CTD pump probs
1836	27 39.3N 23 22.2W CTD redeployed @ Station T22 IN
1924	CTD recovered
2030	27 37.1N 23 24.6W CTD deployed @ Station T23 IN
2122	CTD recovered
2155	27 37.0N 23 24.0W Commence UOR deployment
2158	UOR recovered due to fault & proposed run subsequently cancelled
2210	27 36.9N 23 24.6W Commence non-toxic mapping run @ 8 knots
2004-05-12	
0007	2741.9N 23 20.5W A/c to 057 degs, continuing mapping run
0359	27 39.7N 23 22.1W Complete mapping & hove-to off Drifter
0402	27 39.8N 23 22.1W CTD deployed @ Station T24 IN
0442	CTD recovered
0702	27 39.8N 23 22.1W CTD deployed @ Station T25 IN
0802	CTD recovered; processing & reviewing
1028	27 39.8N 23 21.7W Deploying UOR; TMS deployed
1150	27 40.8N 23 20.2W UOR recovered; v/l repositioning
1217	TMS recovered
1301	27 39.9N 23 22.0W Optics rig deployed
1351	27 40.0N 23 21.5W Optics rig recovered
1410	27 39.9N 23 21.6W CTD deployed @ Station T26 IN
1440	CTD recovered; v/l steaming 180 degs x 20 nm to clear area
1650	27 18.3N 23 20.7W V/l hove-to; scientists @ leisure
2400	27 22.6N 23 17.6W V/l making 1 – 2 knots, NxW heading
2004-05-13	
0700	27.38.1N 23.07.0W Set co. 282 dees towards work area
1018	27 42 1N 23 25 6W Hove-to off Drifter 'D'
1110	27 42.1N 23 25.2W Optics rig casts
1145	Optics casts completed
1200	27 42 6N 23 25 3W CTD deployed @ Station T27 IN
1308	CTD recovered
1408	V/l repositioning
1615	27 45 0N 23 23 8W CTD deployed @ Station T28 IN
1720	CTD recovered
1810	27 45.3N 23 23.5W UOR deployed for trials @ various depths & v/l speeds
1956	UOR recovered
2006	27 49.6N 23 27.2W TMS deployed
2058	27 45.7N 23 26.9W Deploying UOR; tows to Sci req. in patch vicinity o'night
0004 05 44	
2004-05-14	07 00 0NI 00 14 0NI
0240	27 30 3N 23 14.2VV
0.428	27 30.0NL 23 18.2W UUK recovered
0428	27 26 ONL 22 16 2007 CTD download @ Station T20 INL
0430	27 30.91N 23 10.2VV UTD deployed @ Station 129 IIN
0500	CID recovered
0020	Steaming outwith site
UDJU 0719	27 ONL 22 16 200 CTD dominant of Station T20 IN
U/1ð 0021	CTD recovered
0031	

1114 27 37.2N 23 16.3W Optics rig casts

11	53	Casts completed
120	06	27 38.0N 23 16.4W CTD deployed @ Station T31 IN
130	00	CTD recovered
134	45	27 40.8N 23 12.2W Approaching 'Poseidon' for small boat transfer
140	00	Boat leaving 'Poseidon'
14	15	27 40.9N 23 12.1W Transfer completed – 1 off, 1 on
14	50	27 41.2N 23 11.5W CTD deployed @ Station T32 OUT
150	00	Safety briefing completed for newly joined Scientist
154	40	CTD recovered
170	00	27 40.9N 23 12.2W RIB launched for personnel return after meeting
172	25	RIB recovered
190	04	27 42.7N 23 26.2W Drifter grappled & recovered
202	25	27 38.1N 23 17.2W Commence non-toxic o'night mapping survey
<u>200</u>	<u>04-05-15</u>	
00.	15	27 35.6N 23 14.2W
042	27	27 36.8N 23 14.5W Hove-to @ completion of survey
07.	14 07	27 36.91N 23 14.3W CTD deployed @ Station 133 IN
087	25	CID recovered
090	00 20	RIB launched to collect equipment from Poseidon
09.	50 59	RIB recovered
114	52 20	27 37.01 23 15.0W Continuing Elward @ 10 linets
11.	59 50	27 57.41 25 06.9W Continuing E Ward @ 10 knots
11	00 27	ADCF IIItel-calibration with roseluon 27.27.2N 22.20.9W Hove to @ NE corner of new Datch survey 'boy'
14	37 A A	27 37 2N 22 39.6W THOVE-ID @ INE COILIEI OF HEW FAILIT SUFVEY DOX 27 37 2N 22 30 7W/ CTD deployed @ Station D1
14	44 10	CTD recovered
16	10	27 32 3N 22 34 3W/ CTD deployed @ Station P9
165	29	CTD recovered
175	20 21	27 27 4N 22 28 6W CTD deployed @ Station P5
17	50	CTD recovered
19	12	27 37 2N 22 28 6W CTD deployed @ Station P3
195	35	CTD recovered
202	27	27 37.3N 22 34.3W CTD deployed @ Station P2
20	53	CTD recovered
22	16	27 27.2N 22 34.3W CTD deployed @ Station P6
224	42	CTD recovered; v/l 'dodging' o'night south of P9
<u>200</u>	<u>04-05-16</u>	
043	35	27 32.4N 22 34.3W CTD deployed @ P9: Station TB000
053	37	CTD recovered
06	58	Commence FRRF Dhan Buoy deployment
07	12	27 32.5N 22 34.2W FRRF Buoy released: Bcn 'C' (003)
074	40	27 32.8N 22 34.2W Drifter Buoy 'D' (004) released with thermistor string
08	51	27 32.7N 22 34.0W 'D' recovered to deck
08	55	27 32.7N 22 34.0W Re-released as 'A' (001)
10	18	27 32.5N 22 34.2W Depressor wt. and patching hose deployed
130	00	27 33.0N 22 33.6W Commence patch deployment (ferrous sulphate) @ 2 knots;
		expanding square courses from buoy 'A'
184	43	27 33.9N 22 32.8W Patch laying back towards buoy 'A'
190	00	27.33.4N_22.32.2W_Patch laying outward in expanding square

190027 33.4N22 32.2WPatch laying outward in expanding square232227 33.1N22 29.9WPatch laying complete; recovering pipe & gear

2004-05-17

- 0230 27 31.6N 22 30.3W 'Dodging' clear of patch
- 0350 Closing buoy positions
- 0415 27 22.8N 22 30.0W CTD deployed @ Station TB001
- 0447 CTD recovered; mapping survey, 'boxing-in' Drifter
- 0628 27 34.5N 22 28.4W Heading for Drifter position
- 0704 27 33.2N 22 29.5W Hove-to & CTD deployed @ Station TB002
- 0806 CTD recovered
- 0835 PES deployed; Commence mapping survey
- 1257 27 33.8N 22 28.0W Complete mapping & hove-to for Optics/CTD
- 1355 Optics measurements completed
- 1359 27 34.2N 22 27.4W CTD deployed @ Station TB003
- 1459 CTD recovered; preparations for over-patching
- 1604 Deploying depressor & pipe
- 1719 27 34.1N 22 27.5W Commence overpatching with phosphate; 2 knots; expanding square

2004-05-18

0200	27 34.3N 22 24.2W Patching continues
0800	27 35.7N 22 22.1W
1200	27 38.0N 22 21.3W
1530	27 39.2N 22 23.2W Overpatching complete; recovering depressor gear
1600	Initial mapping
1725	27 41.2N 22 23.1W Heading for Dan buoy 'C'
1819	27 36.0N 22 23.2W Dan buoy & gear recovered; heading for Drifter 'A'
1900	27 36.3N 22 22.3W PES recovered
1913	27 36.2N 22 22.2W Drifter & thermistor array recovered; v/l repositioning for
	re-deployment
1942	27 38.4N 22 22.4W FRRF gear & Dan buoy ('C') redeployed; v/l repositioning
2002	27 38.8N 22 22.3W Drifter 'D' deployed
2026	TMS re-deployed
2103	27 38.9N 22 22.4W Commence mapping survey; expanding square @ 8 knots
9004 05 10	
<u>2004-05-19</u>	97 40 9NI 99 10 0NI
0000	27 40.21N 22 19.9W
0418	27 39.31 22 19.3W HOVE-10 & TWS recovered 97 20 2N 22 10 2W CTD depleyed @ Station TD004
0424	27 59.51V 22 19.5VV CTD deployed @ Station Tb004
0404	27 20 AN 22 18 7W CTD deployed @ Station TP005
0720	27 59.41 22 18.7W CTD deployed @ Station 16005
0030	CID recovered
0938-1030	27 40 EN 22 16 OW Commence antice manufacture
1114	27 40.51N 22 16.9W Commence optics measurements
1100	27 40.4N 22 10.7W Complete optics measurements 97 40 5N 99 16 7W CTD deployed @ Station TD006
1208	27 40.51N 22 10.77V CTD deployed @ Station 16000
1252	CID recovered; set co. for out station
1450	27 40.4N 22 23.2W CID deployed @ Station 1B007
1542	CTD recovered
1000-1017	Opucs measurements
1620	Security Awareness Briefing followed by Stowaway & suspicious packages
1819	97 10 1N 99 99 8W/ CTD deployed @ Station TROOS
1012	CTD recovered
2007	27 40 9N 22 22 9W UOR deployed & commence N/S tracks survey @ 8 knots
~~~	

2045	27 39.9N 22 22.0W UOR tow shortened; speed to 2 knots
2053	TMS deployed
2105	27 38.3N 22 21.8W Resume UOR mapping tow @ 8 knots
2004-05-20	
0330	27 41.1N 22 14.9W UOR recovered: repositioning for CTD
0415	TMS recovered
0427	27 38.6N 22 16.0W CTD deployed @ Station Diel01
0450	CTD recovered
0650	27 38 6N 22 15 1W CTD deployed @ Station Diel02
0705	CTD recovered
0810	27.38.4N 22.15.0W CTD deployed @ Station Diel03
0915	CTD recovered: shift location relative to 'C' buov
1019	27 38 4N 22 14 4W CTD deployed @ Station Diel04
1036	CTD recovered
1150	27.38.2N 22.13.8W Co Var to Sci Reg – seeking natch centre
1401	27 40 7N 22 13 0W CTD deployed @ Station Diel05
1433	CTD recovered
1452-1538	Optics measurements
1608	27 40.7N 22 12.6W CTD deployed @ Station Diel06
1647	CTD recovered
1806	27 40.7N 22 12.6W CTD deployed @ Station Diel07
1841	CTD recovered
2006	27 40.8N 22 12.6W CTD deployed @ Station Diel08
2036	CTD recovered
2206	27 41.1N 22 12.2W CTD deployed @ Station Diel09
2228	CTD recovered
2004-05-21	
0005	27 41.6N 22 11.8W CTD deployed @ Station Diel10
0020	CTD recovered
0146	27 41.5N 22 11.5W Commence 'bow tie' mapping survey to locate Patch centre
0359	27 40.1N 22 13.1W Hove-to @ completion of survey
0408	27 40.1N 22 13.3W CTD deployed @ Station Diel11
0443	CTD recovered
0517	27 40.1 N 22 12.7 W Conducting short survey
0706	27 40.3N 22 12.7W CTD deployed @ Station TB09 IN
0806	CTD recovered
0842	Proceeding towards Dan buoy ('C') rig for recovery
0953	27 42.0N 22 07.7W Dan buoy & rig recovered to deck; v/l returning to station
1104-1132	Optics measurements
1137	27 40.4N 22 12.6W CTD deployed @ Station TB10 IN
1217	27 40.2N 22 12.3W CTD recovered
1305	27 40.1N 22 11.8W RIB launched to exchange samples with 'Poseidon' for
1000	cross-calibration exercise
1355	27 40.1N 22 11.1W Exchange complete: RIB recovered: re-establishing Drifter
	position.
1457	27 41.22N 22 11.19W FRRF 'C' rig re-released. 1.88nm SWxS of 'D'
1500	V/l w'bound for 5nm
1557	27 41.1N 22 16.8W CTD deployed @ Station TB11 OUT
1650	CTD recovered: v/l positioning for mapping survey
2011	27 41 5N 22 14 6W TMS deployed

27 41.5N 22 14.6W TMS deployed 2029 27 41.6N 22 13.0W UOR deployed; commence mapping run

#### 2004-05-22

- 0000 27 40.2N 21 57.0W
- 0630 27 40.5N 22 04.5W UOR recovered
- 0645 TMS recovered; re-positioning for CTDs
- 0714 27 42.1 N 22 03.5 W CTD deployed @ Station TB12 IN
- 0816 CTD recovered
- 1030 N'bound for 5 nm
- 1110 27 47.3N 22 03.3W Optics measurements
- 1129 Measurements complete
- 1138 27 47.2N 22 03.1W CTD deployed @ Station TB13 OUT
- 1206 CTD recovered; v/l proceeding for buoy recoveries
- 1317 27 44.9N 22 05.9W 'D' grappled
- 1323 'D' rig inboard
- 1350 27 43.6N 22 06.5W 'C' grappled
- 1354 'C' rig inboard; Science completed; Set co. for Tenerife @ 110 rpm
- 2000 27 46.7N 21 00.5W Incr. to 120 rpm (poss. medical case).

#### 2004-05-23

- 0000 27 49.3N 20 12.4W
- 0200 Clocks advanced 1hr to UTC +1
- 0700 27 53.3N 28 44.8W
- 1100 27 55.9N 17 55.7W Pta Norte brng 181 degs x 4.8 nm
- 1500 27 56.5N 17 06.7W Pta de San Cristobal brng 006 degs x 9.2 nm
- 2000 Pta Perfecto brng 298 degs x 3.15 nm
- 2100 28 25.7N 16 14.1W All critical Bridge/ER equipment tested & satisfactory
- 2106 EoP; ERSB; Sur B'water brng 357.5 degs x 2.6 nm
- 2122 PoB Morales
- B'waters abeam to P&S
- 2157 Spring ashore for'd
- All fast F&A; RFWE

# **PATCH DEPLOYMENT/CREATION**

## *Tim Fileman*

When it came, the move through 12 orders of magnitude from working in nanograms to tonnes wasn't as painful as I'd first thought. My brief was to find a way of seeding a patch of ocean (possibly up to 49 km²) with as much phosphate as possible and some iron (Ferrous Sulphate). This meant finding a chemical form of phosphate which was very soluble in seawater, produced PO_{4³⁻} in solution and maximised the PO_{4³⁻} available. We finally settled on 40 tonnes of monosodium phosphate anhydrous (MSP) which is a common food additive and is produced in vast quantities in Israel. The next challenge was how to get the stuff, which comes in 25kg bags (That's 1600 bags!) into solution on the ship so we could mix it with a tracer (SF $_6$ ) and pump it into the ocean. My search for a solution (sorry!) lead me to a device called a flexible screw conveyor (the silver thing with the white tube in front of the tanks below). It uses a rotating flexible spring-like screw to push the powder (at 2 tonnes per hour) up the white tube and into the tanks below.



Assembling the tank system with the Flexible Screw Conveyor.

Experiments in the laboratory (in a 2 litre beaker) showed that at 20°C it should be possible to get 1.5 tonnes of MSP into 3000 litres of seawater if it's dissolved over a period of about an hour. Allowing for a pumping rate of 2500 litres per hour and some expansion due to the quantity of powder added, two 3500 litre plastic oil tanks where purchased. I designed, and had built, a frame to hold the tanks in place on the deck of the ship and to support the two tanks stirrers. All this only came together literally just before we stuffed the containers to ship the gear out of PML. The first time I would see the whole apparatus together and working would be on the ship on the way out to the working area off the Canaries.



a) Loading 45 one tonne pallets of MSP & Ferrous Sulphate in Santa Cruz; b) Loading 25kg bags of powder into the conveyor.

Teams were organised to work 4 hour shifts loading powder into the tanks. The first 25 km² phosphate patch was deployed almost without a hitch in 24 hours. This was followed later

with another patch in which we laid 5 tonnes of ferrous sulphate and overlaid it with a further 20 tonnes of MSP. The MSP and ferrous sulphate were loaded in batches of 6 bags roughly every 10 minutes. Each tank took about 1.5 hours to pump out so there was plenty of time for a "smoko" between tanks.



a) SF₆ saturation system with tanks and the pumping system on the right; b) View into a tank of seawater with 1.5 tonnes of MSP being stirred in; c) The ferrous sulphate heptahydrate needed to be added to acidified seawater to keep the iron as  $Fe^{2+}$  (pH 2 after addition of 2.5 litres of concentrated sulphuric acid); d) pH before and after acidification.

The patch centres were marked with DML type drifter buoys (Compass Hydrographic Ltd) which feed GPS data (along with GPS from the ship) every two minutes into our PatchDeploy software. The PatchDepoly software facilitated the laying of our patch relative to the movement of the sea and not the ground. Waypoints in our deployment pattern are updated relative to the movement of the buoy as the ship moves through the deployment grid. After deployment of the patch the buoy was replaced with an Argos equipped version which sent GPS every 5 minutes. Please refer to Ricardo Torres' report for the drifter buoy data.



Assembling a drifter buoy with a 180 metre long thermistor chain attached.

### PHYSICAL OCEANOGRAPHIC CONDITIONS DURING FEEP

## Ricardo Torres

## Aims and objectives

A set of measurements were routinely taken during CD156 to enable the description and interpretation of the physical oceanographic conditions during the experiments. The aim is to quantify the upper layer physical variability mainly in terms of local currents and hydrography (water temperature structure in particular) to help in the interpretation of the background conditions and evolution of the released patches. Particularly, it aims at separating physical from biological effects on the patch evolution of releases. Four instruments were used to that end, a Lowered Acoustic Doppler Current Profiler (LADCP), an Acoustic Doppler Current Profiler (ADCP), a set of Argos drifters and a thermistor chain.

## Lowered acoustic doppler current profiler

During the CD156 cruise a Lowered Acoustic Doppler Current Profiler (LADCP) RDI 300kHz was mounted on the 24 bottle CTD frame. The system was routinely used in all CTD casts in a downward looking configuration. The LADCP was setup with a 1s ping cycle, 10m cell length, a 5m blank, 16 bins and 1 ping per ensemble. After initial trials, the number of bins was reduced to 10bins as no good bins were being recorded beyond that. The configuration commands used in each deployment were:

# CF11101, EA00000, EB00000, ED00000, ES35, EX11101, EZ0111101, TE00000100, TP000000, LD111100000, LF0500, LN010, LP00001, LS1000, LV150, LJ1, LW0, LZ30,220, SM0

The system was lowered to a maximum depth of 500m and occasionally to shallower depths depending on time availability. On no occasion was the LADCP deployed to the seafloor and hence no bottom tracking pings were used. The data were processed onboard using the well established software developed by Eric Firing at the University of Hawaii (Firing, 1998). Overall the data obtained during the cruise was of good quality. On average, 100 return samples were recorded at depth, increasing to over 500 in the top 100m where the bottles were being fired. Only on CTD cast 004 the LADCP was not operated. The LADCP connector to the star cable was at fault and no power was being supplied to the unit. The power supply was rerouted inside the star cable to a different wire and no further problems were encountered.

LADCP files were recovered after each cast and ftp across to the ship's networked Unix machines to a laptop for post-processing. The steps involved included the inspection of the raw data for consistency with the LADCP logsheets (e.g. depth, up and downcast times); the extraction of navigation data from the ship system and merging with the LADCP raw data; calculation of correction to the direction of the LADCP velocities based on the local magnetic declination; merging of raw data into single up and down cast, and preliminary estimation of bin depths by integration of the measured vertical velocity. First estimates of absolute velocities were then calculated by removing the vertical and horizontal measurement of the CTD frame. The last step is to calculate depth varying sound speed with the CTD data, recalc ulate LADCP velocity estimates, refine depth bins from the CTD pressure data and update the final absolute velocities. Comparison of VMADCP and LADCP data showed good correspondence between both data sets.

## Vessel-mounted acoustic doppler current profiler (VMADCP)

During the cruise, data from the vessel-mounted (VM-) 150 Hz RDI Narrow Band ADCP were collected throughout. Data was collected with RDI DAS software and output as RDI pingdata. Navigation information from the TRIMBLE 4000 was merged with ADCP data in real-time with the use of the user exit program UE4 from the University of Hawaii. The software also ensures that the PC is always synchronised with the navigation time. The period of data collection was between 05:00 21 April to 14:00 23 May 2004.

DAS software was set to collect with the following main parameters:

- No bottom tracking
- Heading compensation
- 300s averaging interval for ensembles
- 24 bins of 8m
- blank beyond transmit was set to 8m
- Use of 3 beam solution

During the first few days of the cruise it became apparent that pings from Beam 3 were of significantly worse quality than the other beams. On average, Beam 3 recorded less than 50% good pings (sometimes as low as 5% in over 300 ensembles) compared to over 90% recorded by the other Beams. This caused error velocity estimates to be higher than expected and as a consequence reasonable data was being flagged as bad, lowering the Percentage Good and not being processed by DAS. The origin of Beam 3 problems was not identified and it was decided not to use the error velocity as a quality control parameter as means of diminishing the number of data loss and the 3 beam solution was enabled. As a consequence, data quality increased. The average number of pings processed by DAS was 270 pings per ensemble.

Ashtech ADU-GPS needed for correcting the ship's gyrocompass was only recorded between 15:00 6 May 2004 and 11:00 9 May 2004. Outside these dates, technical problems prevented the use the instrument. A calibration leg of 1 hour 45 min was performed with Posidon. It consisted of both ships steaming along side at a constant heading and speed from 11:35 to 13:15 15 May.

On 11 May 2004 the ADCP stopped functioning. All four beams were failing the Built In Test (BIT) with Spectral Width, Signal and Frequency errors. RDI diagnostic software VMTEST was used to identify the origin of the problem. In addition to failing the BIT test, both the Pre-amplification and Continuity and Isolation test also failed. Without direct access to the system, the ADCP was off line until the 14 May. The ADCP pool was then purged of built up air pressure and the errors disappeared. The ADCP continued to give reasonable data until the end of the cruise.

The ADCP data were processed onboard using the Common Oceanographic Data Access System (CODAS), developed at the University of Hawaii by Eric Firing and Ramon Cabrera with subsequent updates by Julie Ranada (Firing *et al.*, 1995). The system consists of several iterative C and matlab programs to carry out editing, calibration, navigational correction and plotting of the ADCP database. The principal objectives of the editing stage are to identify and flag bins showing erroneous data caused by interference from physical objects, such as the winch wire during a CTD cast or air bubbles caused by rough weather. Velocities relative to the ship must be adjusted for orientation of the transducer relative to the gyro compass and for any inaccuracy in the relative geometry of the four beams. With accurate navigation information available during large changes in ship's velocity, amplitude and angle errors can be computed from the ADCP. The method used was water track, which compares the acceleration relative to the water, measured with the ADCP, to the acceleration over the ground, calculated from navigation. The calibration consists in the calculation of the amplitude and phase (angle) correction factor to the water track velocities to be used subsequently in the Gyro correction. The amplitude factor correction was found to be 1.009 and the phase was -3.12°.

The final step in processing ADCP data is introducing the navigation data, which are used to calculate the ship's velocity and absolute water velocities. The absolute reference layer velocity is the sum of the ship's speed over the ground obtained from the navigation data, and the average relative water velocity in the reference layer, measured by the ADCP. This layer is calculated with reference bins between 5 to 20. The data used in this interval have a percentage good over 30. Once the reference layer is obtained the data are interpolated and

smoothed. Profile positions are then recalculated from the smoothed velocities. The final estimate of true velocities is made by adding the difference profile from the reference layer velocity, to the final absolute reference layer velocities. The steps followed in this process were:

- 1. Obtain the ship velocity relative to the reference layer.
- 2. Calculate the absolute ship velocity.
- 3. Smooth and interpolate the data to the ADCP ensemble times.
- 4. Update the database.



Figure 1 Example of ADCP vector plot during survey 2 (6 May 14:00 to 7 May 08:00 2004). Data from 30 to 50m have been averaged vertically and spatially every 0.02 degrees latitude and longitude.

Example of processed ADCP data is shown in Figure 1 in the form of a gridded vector plot. The apparent velocity divergences in the plot are related to the presence of inertial waves. This will be filtered out in further post processing to yield fields of residual currents. The ADCP generally performed well underway during the overnight UOR tows generally reaching maximum depths of 180m.

## Drifter data

Dunstaffnage Marine Laboratory type ARGOS and GPS tracked buoys (Compass Hydrographic Ltd) were deployed during CD156 to mark the centre of the two patches. They consisted of a surface buoy with the GPS and ARGOS transmitters and the battery pack. All the buoys were drogued at a nominal depth of 20 metres with a 2m long, 1.5m diameter Holley Sock type drogue. The buoys were set to transmit every 2min during the patch releases and every 5min afterwards. The GPS data were continuously logged on a Laptop. The data were averaged into 5 min, filtered for spikes in the position fixes and interpolated using a spline function to 15min intervals. In the first release experiment only one drifter buoy was tracked. It carried a 180m thermistor's chain. In the second release two buoys were deployed and tracked simultaneously, one with the thermistor chain and another with a Fast Repetition Rate Fluorometer (FRRF) at 26m depth. The sequence of buoy deployment, tracking and recovery during the cruise is summarised in Table 1.

*Table 1 Drifters deployment and recovery times during both patch releases. Bold T indicates drifter with thermistor chain.* 

Release Ex	<b>Buoy ID</b>	Deployment	Recovery	Comment	
PO4	D- <b>T</b>	4-May 15:27	10-May 20:00	Recovered for reposition at patch	
				centre	
PO4	C	10-May 19:54	11-May 16:06	Temporal patch centre marker	
PO4	D- <b>T</b>	10-May 23:37	13-May 13:00	End of PO4 release experiment	
PO4+Fe	D- <b>T</b>	16-May 08:00	16-May 09:30	Changed with buoy A to get	
				positions every 2min instead of	
				5min.	
PO4+Fe	A- <b>T</b>	16-May 09:30	18-May 19:10	Recovered and changed by buoy	
				D. Reposition in patch center.	
PO4+Fe	C	16-May 07:30	18-May 18:30	FRRF buoy. Reposition in patch	
				center.	
PO4+Fe	D- <b>T</b>	18-May 20:00	22-May 13:15	End of release 2 experiment	
PO4+Fe	С	18-May 19:50	22-May 13:45	FRRF buoy. End of release 2 expt	

During the first release experiment (Figure 2), the buoys experienced strong inertial oscillations with a 25.9 hour period. The oscillations were superimposed in a slow anticyclonic circulation. Maximum speeds were of the order of 15-20cm/s.



*Figure 2 Drifter tracks during first patch experiment. The different colours indicate change of drifters. Year day overlaid on the tracks are every 12 hours.* 



Figure 3 Drifter tracks during the first day of the Iron and Phosphate patch monitoring.

During the second patch experiment (Figure 3), inertial oscillations were still present but were much weaker than before. The background flow was E-NE for the duration of the deployment. Averaged mean flow was 10cm/s. The drifters showed a larger slippage with respect to the SF6 patch when compared to the first release experiment. Increased solar insulation and low winds caused the top 50m to stratify, generating vertical shear in the horizontal velocities and decoupling the drifter's behaviour from the SF6 patch evolution. The slippage was of the order of 1 km a day. Both FRRF and thermistor drifter behaved relatively similar in low wind conditions.

#### Thermistor data

During both patch experiments, a drifter with a 180m long thermistor chain was deployed and tracked throughout. The chain consisted of a combination of 10 Vemco temperature miniloggers, 4 Richard Brancker Research (RBR) TR-1050 temperature loggers and 4 RBR TDR-2050 temperature and depth loggers. The configuration during each deployment is summarised in Table 2 and 3.

Table 2 Thermistors chain configuration during first patch release	se. RBR denotes temperature only recorder while
RBRD denotes temperature and pressure recorder.	

Depth	Туре	ID
5	RBR	11410
10	RBRD	11765
20	Vemco	9726A
30	RBR	11408
40	RBRD	11766
50	RBR	11409
55	Vemco	9764A
60	RBRD	11768
65	Vemco	9709A
70	RBR	11406
80	RBRD	11767
100	Vemco	9767A
120	Vemco	9757A
130	Vemco	9771A
140	Vemco	9754A
150	Vemco	9732A
160	Vemco	9718A
170	Vemco	9739A

Table 3 Thermistors chain configuration during second patch release. RBR denotes temperature only recorder while RBRD denotes temperature and pressure recorder

Depth	Туре	ID
5	RBR	11410
10	Vemco	9726A
20	Vemco	9764A
30	Vemco	9739A
40	RBRD	11766
50	Vemco	9709A
60	RBR	11409
70	RBRD	11768
80	RBR	11406
90	RBRD	11765
100	Vemco	9767A
110	RBR	11408
120	Vemco	9757A
130	Vemco	9771A
140	Vemco	9754A
150	Vemco	9732A
160	Vemco	9718A
170	RBRD	11767

All loggers collected good quality data throughout the deployments. During the first deployment (Figure 4 and Figure 5), above 30m, surface waters were subject to solar heating, with a maximum on 7 May and minimum on 9 May and increasing again towards the end of the release. Below 40m, temperature decreased during the day due to mixing with lower waters, while increasing during the night as a result of night time convection. Night time convection was present throughout the deployment reaching a maximum depth of at least 80m on 12-13 May (Figure 5).



*Figure 4 Time evolution of the temperature in the top 80m from the RBR thermistors during the first five days of deployment in Patch 1.* 



Figure 5 Time evolution of the temperature in the top 80m from the RBR thermistors during the last four days of deployment in Patch 1.

During the second release (Figure 6), stronger stratification was present in the top 80m than in the previous deployment. The top meters showed a daily increase in temperature of 0.5°C, more than twice that in the previous release due to a shallower mixed layer. The low winds conditions favoured a steady increase in temperature in the top layer (at least above 40m) of 0.5°C during the length of the deployment and a similar decrease below 80m. Night time convection was weaker than in the previous release and became less apparent towards the end of the deployment.



Figure 6 Time evolution of the temperature in the top 170m from the RBR thermistors during deployment in Patch 2.

#### **References**

E. Firing. Lowered ADCP and use in WOCE. *International WOCE Newsletter*. p 10-15, 1998.

Firing, E., J. Ranada, and P. Caldwell, *Processing ADCP Data with the CODAS Software System Version 3.1, User's Manual*, University of Hawaii, 1995.

#### SULPHUR HEXAFLUORIDE MEASUREMENTS *Phil Nightingale & Tim Fileman* Objectives:

The aims of the SF6 measurements during FEEP were:

- 1. To provide a framework for the 1) phosphate and 2) iron and phosphate addition experiments by the release of SF6 simultaneously with the phosphate in the first experiment and with the iron in the subsequent experiment. The tracer could then be used to re-locate the region of water that was influenced by the added phosphate and iron and phosphate, and provide a proxy for the nutrients when no longer detectable
- 2. To enable the rates of dilution and spreading affecting the mixed layer water to be measured in both horizontal and vertical directions. These measurements will be related to the physical processes forcing mixing.

## **Methodology:**

Two fully automated GCs systems were refurbished by Phil Nightingale, Malcolm Liddicoat and Hester Wilson prior to the FeeP cruises. New electronic control systems, valving, cyrotrapping units and labview software were employed such that both the system on the Darwin and the system on Poseidon could be used in either an underway mapping mode or in a discrete mode for conducting vertical profiles. Despite some intial teething problems both systems were successfully used for the whole period of the cruise. The Darwin system was typically used in underway mode from about 17-00 hrs through to the pre-dawn cast at 03-00hrs. It was often left running during the series of casts in the morning both as a check on whether the vessel was still in patch centre and also to allow comparison with samples collected via the CTD rosette. It was also used in underway mode for short periods during the day in order to reposition the vessel within the tracer patch (see record in Table 1 below). Discrete measurements were taken from almost every station and typically from each of the individual dips (see record in Table 2 below).

The underway methodology more or less followed that of Upstill-Goddard ewt al. 1990 and as updated in Nightingale et al. 2000. Samples were collected fron the ship's pumped seawater supply and analysed every three minutes via purge and trap gas chromatography and displayed on a near real time (total delay 5 minutes) map after interfacing with a GPS stream. Discrete SF₆ samples were sub-sampled into 500ml glass stoppered bottles from the sampling rosette. The SF₆ was removed by sparge-cryotrapping, isolated chromatographically and detected by electron capture dectector, following much of the methodology described in Law et al, 1994. Measurements were calibrated against standards prepared by the Volatiles group at PML and an inter-calibration of samples between the systems on Darwin and Poseidon was undertaken. Comparison of the analyses made whilst the GC was operated in underway mode with samples collected at the same time and run in discrete mode showed that the underway system was 85& efficient and the final underway data have therefore been corrected.

### **Preliminary results:**

A summary of preliminary results is given below.

Survey	Start Date/Time	Finish Date/Time	Upper	Comments
			Percentile	
			(fmol dm ⁻³ )	
1	06/05/2004 00:47	06/05/2004 04:17	553	Patch 1
2	06/05/2004 15:55	07/05/2004 07:42	554	
3	07/05/2004 21:38	08/05/2004 10:39	572	
4	08/05/2004 17:23	09/05/2004 07:25	425	
5	09/05/2004 13:55	10/05/2004 08:16	293	
6	11/05/2004 22:09	12/05/2004 04:41	88.1	
7	13/05/2004 13:59	14/05/2004 07:20	128	
8	14/05/2004 20:16	15/05/2004 06:54	85.2	
1	17/05/2004 03:37	17/05/2004 12:48	1730	Patch 2: Fe Only:
2	17/05/2004 16:49	18/05/2004 17:55	1070	PO ₄ deployment
3	18/05/2004 21:28	19/05/2004 07:03	1050	
4	19/05/2004 20:03	20/05/2004 04:24	255	
	20/05/2004 11:45	20/05/2004 13:54		transect
5	21/05/2004 01:46	21/05/2004 07:08	237	
6	21/05/2004 20:13	22/05/2004 07:28	112	

Table 1: Underway Sampling Periods

Note: System may be been running whilst on station so times do not necessarily reflect start and finish of mapping surveys.

## Table 2: Stations/casts analysed

					Patch	SF ₆	SF ₆	
Date	Time	Cast	Description	In/Out	Centre	mixed denth	Penetrat. Denth	Comment
			Patch 1			ucpui	Depth	
04/05	08:43	D29	Pre-release	n/a				Slight contamination
05/05	19:13	D30	T1 in	IN	Ν	15	40	0
								samples stored 24
06/05	07:15	D32	T3 in	IN	Y	3	50	hrs
07/05	07:45	D34	T5 in	IN	Y	26	50	
07/05	13:29	D35	T6 in	IN	Y	26	50	
07/05	15:51	D36	T7 out	OUT				
08/05	10:45	D37	T8 in	IN	Y	50	60	
08/05	15:48	D38	T9 out	OUT				
09/05	04:30	D39	T10 in	EDGE				
09/05	07:26	D40	T11 in	IN	Ν	55	65	
09/05	12:40	D41	T12	EDGE				Slight edge
10/05	07:36	D43	T14 in	IN	Y	60	60	
10/05	12:30	D44	T15 in	IN	Ν			
10/05	14:30	D45	T16 out	OUT				
11/05	06:15	D46	T17 Transect 1	IN	Ν	70	80	
11/05	08:45	D47	T18 Transect 1	OUT				
11/05	11:00	D48	T19 Transect 1	IN	Ν	60	70	
11/05	13:00	D49	T20 Transect 1	IN	Ν	65	70	
11/05	14:13	D50	T21 Transect 1	EDGE		10	65	low SF ₆ 26 - 50m
11/05	18:30	D51	T22 Transect 1	EDGE		10	65	low SF ₆ 26 - 50m
11/05	21:30	D52	T23 Transect 1	OUT				
12/05	07:04	D54	T25	IN	Ν	80	100	
12/05	13:50	D55	T26	OUT				supposed to be in?
13/05	12:10	D56	T27	EDGE				
13/05	17:15	D57	T28	IN	Ν	60	100	
14/05	08:30	D59	T30	IN	Y	60	90	
14/05	05:30	D58	T29	IN	Y			
14/05	12:00	D60	T30	IN	Y	60	90	

14/05	15:00	D61	T31	OUT			
15/05	07:16	D62	T32	IN	Y	40	95
			Patch 2				
16/05	04:34	D69	pre-release	n/a			
17/05	07:10	D71	Tb 2	IN	Y	26	30
19/05	07:10	D74	Tb 5	IN	Y	26	26
19/05	04:00	D73	Tb 4	IN	Y		
19/05	14:40	D76	Tb 7	OUT			
19/05	12:07	D75	Tb 6	IN	Ν	10	
20/05	04:40	D78	diel1	IN	Ν	3	26
20/05	06:40	D79	diel2	IN	Ν	3	26
20/05	08:10	D80	diel3 Tb 8	IN	Ν	3	10
20/05	10:20	D81	diel4	IN	Ν	3	<26
20/05	12:00	D82	diel5	IN	Y	3	>26
20/05	16:08	D83	diel6	IN	Y	3	>26
20/05	18:05	D84	diel7	IN	Y	3	>26
20/05	20:06	D85	diel8	IN	Y	>26	
20/05	22:06	D86	diel9	IN	Ν	3	>26
21/05	00:20	D87	diel10	IN	Ν	3	>26
21/05	07:06	D89	diel 12 Tb 9	IN	Ν	3	30
21/05	04:10	D88	diel11	IN	Ν	3	>26
21/05	11:40	D90	Intercalibration	IN	Ν	3	30
22/05	07:15	D92	Tb 12	IN	Ν	3	30
21/05	16:00	D91	Tb 11	OUT			
22/05	11:37	D93	Tb 13	OUT			
			_	-			

NB: Edge = < 10% of survey max. Patch centre = upper 10 precentile of survey

## **Darwin/Poseidon Intercomparison**

The intercomparison between the Posiedon and Darwin  $SF_6$  instruments showed excellent agreement with a mean difference of just 2.8% between samples analysed on both systems and with different sets of standards.



The SF₆ provided an effective label for the enriched water, providing clear confirmation of whether a Station was IN or OUT. In both experiments samples were analysed for SF6 from the surface, in the mixed layer and through to the pycnocline. Data will be used to improve spatial resolution of the SF₆ distribution for greater accuracy in vertical diffusion (Kz) estimates and underway data will be used to determine horizontal spreading. SF6 will also be used to provide volume and dilution estimates for the patch, and so contribute to the generation of nutrient budgets.

#### **OPTICS & FRRF** *James Richard Fishwick.* Aims

- 1. To measure the photosynthetic properties of the phytoplankton assemblages using the Fast Repetition Rate Fluorometer (FRRF). Assessing any changes due to the addition of the nutrients, Iron and Phosphate.
- 2. Make high quality optical measurements for the determination of possible relationships between the photosynthetic properties measured by the FRRF and optical ratios and for the validation of the satellite sensors MERIS and SeaWiFS in the oligotrophic ocean.
- 3. Particle absorption measurements will be made using a spectrophotometer enabling further determination of any optical relationships with the photosynthetic properties measured by the FRRF.
- 4. Finally pigment samples have been filtered coinciding with all the previous measurements to investigate links with pigment ratios.

## Methods and preliminary results

The FRRF was utilised in several different modes during the cruise, the primary mode was mounted on the CTD/bottle rosette. The FRRF was mounted on the top of the frame preventing any shading on the instrument during the vertical profiles, made to depths of up to 500m. The vertical profiles allowed for the determination of the photosynthetic properties through the water column and for the identification of any biomass maximums. Figure 1 shows a typical FRRF profile over the top 200m of the water column. Showing a Photosynthetically Active Radiation (PAR) light profile used for the determination of percentage light depths. The maximum fluorescence (Fm) is also plotted showing the chlorophyll structure through the water column. The Fm value is very low in the surface mixed layer at around 0.4 increasing to 1.8 in the chlorophyll maximum. This gives a rough indication of the chlorophyll at approximately a quarter of the Fm value. Sigma is plotted giving a value for the cross sectional area of the light harvesting photo-system, this value is typically around 500 - 600 Angstron². Finally the Fv/Fm parameter is plotted, which indicates the photosynthetic quantum efficiency of the phytoplankton. This value is seen to be quenched in the high light surface waters but a value of ~0.4 can be determined for the surface mixed layer from beneath the quenched zone. The Fv/Fm value rises to above 0.5 in the chlorophyll maximum.

The second mode, which the FRRF was used during the cruise, was connected to the non toxic seawater supply during patch mapping through the night. The FRRF was only used in this mode during the hours of darkness to eliminate any ambiguities caused by quenching. The third mode was to mount a second FRRF on a buoy, which was deployed in the centre of the patch before the addition of the Iron and Phosphate. The instrument was suspended below the buoy at a depth of 26m and stayed in the water for three days taking measurements every half an hour. The buoy was then redeployed for the final 24hours of the experiment. From the data collected it will be possible to determine any photosynthetic changes during the nutrient release experiment and also allowing for the calculation of the primary production at 26m throughout each day. This will be calculated using the following formula:

### P(z)= factor * PAR(z) * chl(z) * sigma * Fv/FmL(z)

Optical data was collected using an optical freefall built at the Plymouth Marine Laboratory (PML) utilising a Satlantic Incorporated 7 band Irradiance head and a 7 band Radiance head. The seven wavelengths are comparable with the SeaWiFS sensor and are as follows, 412, 443, 490, 510, 555, 620, and 683nm. The freefall is deployed from the stern of the ship and left to fall independently through the water column at a rate of 0.5m/s. Data is collected from the irradiance head orientated towards the surface and the radiance head measuring up welling light. Ancillary data including the depth and the tilt and roll of the instrument are also

recorded live to a computer on deck via a cable. The PML freefall also has the capability of being used as a surface buoy with the irradiance head being held out of the water with the addition of an extra buoyancy ring. In this form it collects the surface reflection data for satellite validation. Optics log in the appendices number 4.

During the cruise filters were taken for particle absorption measurements, this entails the filters being run on a spectrophotometer, using the Tassan and Ferrari method. Absorption characteristics of both the organic and the inorganic fractions are measured over the full visible spectrum. 4.2litres of seawater was filtered through each filter to provide a sufficient signal for the analysis, this was carried out at three depths; 60m, 26m, and 3m. Samples were collected at each mid-day optics CTD, which was in principal an in patch station and then also at selected out station CTDs. Filters were also collected for the same stations and depths for High Performance Liquid Chromatography (HPLC) pigment analysis. All samples were flash frozen in liquid nitrogen then stored in a -80°C freezer. Logs for both PABS and HPLC are in the appendices number 5.



Figure 1: A typical FRRF cast on CTD 075 a) PAR profile through the water column. b) Fm profile showing the chlorophyll structure. c) Sigma indicates a lower value in the surface mixed layer than in the chlorophyll

maximum. d) Fv/Fm indicating the health of the phytoplankton community through the water column.

Results									
1. FRRF CTD Log									
Cast I.D.	Date	Time	Latitude (N)	Longitude (W)					
CTD156_006	29/04/04	04:02	26 45.26	23 28.09					
CTD156_007	29/04/04	10:10	26 42.68	22 44.00					
CTD156_008	29/04/04	18:38	26 08.23	23 23.83					
CTD156_009	30/04/04	00:47	25 35.93	23 58.61					
CTD156_010	30/04/04	08:20	24 49.31	24 49.60					
CTD156_011	01/05/04	04:42	27 09.66	25 01.78					
CTD156_012	01/05/04	09:59	27 48.30	25 01.20					
CTD156_013	01/05/04	17:56	28 25.08	24 22.45					

CTD156	075	200a	

CTD156_014	01/05/04	23.51	28 38 32	23 37 30
CTD156_015	02/05/04	£0:04 08:38	20 50.52	23 30 70
CTD150_015	02/05/04	00.30	LI J4.24	23 30.79
CTD156_010	02/05/04	17 10	07 50 54	00.00.10
CID156_017	02/05/04	17:18	27 53.54	23 26.16
CTD156_018	02/05/04	21:00	27 58.41	23 19.95
CTD156_019	02/05/04	22:25	27 53.62	23 18.01
CTD156_020	02/05/04	23:40	27 50.18	23 21.92
CTD156_021	03/05/04	01:00	27 46.56	23 26.11
CTD156_022	03/05/04	02:12	27 43.01	23 21.93
CTD156_023	03/05/04	03:29	27 46.65	23 17.95
CTD156_024	03/05/04	04:46	27 50.04	23 14.13
CTD156_025	03/05/04	06:02	27 46.63	23 10.27
CTD156_026	03/05/04	07:12	27 43.10	23 14.19
CTD156 027	03/05/04	08:29	27 39.50	23 18.10
CTD156_028	03/05/04	10:18	27 48.53	23 20.06
CTD156_029	04/05/04	08:43	27 48 77	23 19 83
CTD156_030	05/05/04	19.13	27 47 26	23 18 66
CTD156_032	06/05/04	07:15	27 45 25	23 16 02
$CTD156_032$	06/05/04	19.26	27 45.55	23 10.32
CTD156_034	00/03/04	12.30	27 44.00	20 17.10
CTD156_034	07/05/04	07.43	27 43.30	23 13.22
CTD156_035	07/05/04	13:29	27 44.01	23 13.30
CTD156_036	07/05/04	15:51	27 44.16	23 20.91
CTD156_037	08/05/04	11:12	27 41.01	23 14.24
CTD156_038	08/05/04	15:48	27 41.46	23 02.90
CTD156_039	09/05/04	04:35	27 39.61	23 15.50
CTD156_040	09/05/04	07:34	27 41.48	23 13.77
CTD156_041	09/05/04	12:40	27 42.23	23 13.47
CTD156_042	09/05/04	15:20	27 47.49	23 13.83
CTD156_043	10/05/04	07:36	27 39.47	23 13.24
CTD156_044	10/05/04	12:30	27 40.15	23 13.90
CTD156_045	10/05/04	14:59	27 33.14	23 20.76
CTD156_046	11/05/04	06:09	27 39.89	23 21.27
CTD156 047	11/05/04	08:07	27 42.73	23 18.29
CTD156 048	11/05/04	10:07	27 41.48	23 19.65
	11/05/04	12:12	27 40.69	23 20.35
CTD156_050	11/05/04	14.13	27 39 85	23 21 35
CTD156_051	11/05/04	18:36	27 39 17	23 22 26
CTD156_052	11/05/04	20:32	27 37 08	23 24 58
CTD156_052	12/05/04	04:00	27 30 70	23 22 02
$CTD156_054$	12/05/04	04.09	27 20 20	22 22 15
$CTD150_054$	12/05/04	14:00	27 20 20	22 21 57
CTD150_055	12/05/04	14.03	21 JJ.0J 97 19 01	20 21.01 99 91 70
CTD150_050	13/03/04	12.33	27 44.04	23 24.70
CTD150_057	13/03/04	10:12	۵٦ ۵۵ ۵۸	20 20.0U
CID156_058	14/05/04	04:37	27 36.94	23 16.22
CID156_059	14/05/04	07:19	2/37.02	23 16.35
CTD156_060	14/05/04	12:05	27 37.99	23 16.39
CTD156_061	14/05/04	14:48	27 41.18	23 11.51
CTD156_062	15/05/04	07:16	27 36.93	23 14.29
CTD156_069	16/05/04	04:34	27 32.38	22 34.27
CTD156_070	17/05/04	04:12	27 32.77	22 29.97
CTD156_071	17/05/04	07:04	27 33.24	22 29.54
CTD156_072	17/05/04	13:57	27 34:20	22 27.41
CTD156_073	19/05/04	04:24	27 39.33	22 19.28
CTD156_074	19/05/04	07:21	27 39.42	22 18.74
CTD156_075	19/05/04	12:07	27 40.40	22 16.62
CTD156_076	19/05/04	14:55	27 40.36	22 22.86

CTD156_082	20/05/04	14:00	27 40.67	22 12.95
CTD156_083	20/05/04	16:08	27 40.71	22 12.62
CTD156_084	20/05/04	18:05	27 40.71	22 12.64
CTD156_085	20/05/04	20:06	27 40.77	22 12.63
CTD156_086	20/05/04	22:07	27 41.12	22 12.23
CTD156_087	21/05/04	00:06	27 41.59	22 11.82
CTD156_088	21/05/04	04:11	27 40.12	22 13.28
CTD156_089	21/05/04	07:06	27 40.28	22 12.71
CTD156_090	21/05/04	11:37	27 40.39	22 12.61
CTD156_091	21/05/04	16:00	27 41.20	22 16.85
CTD156_092	22/05/04	07:14	27 42.11	22 03.49
CTD156_093	22/05/04	11:37	27 47.19	22 03.13

#### 2. FRRF Underway Log

File I.D.	Date	Start Time	End Time	Instrument Serial No.
Und_050504	05/05/04	21:10	03:30	CI 18043
Und_060504	06/05/04	22:00	06:20	CI 18043
Und_070504	07/05/04	20:20	06:30	CI 18043
Und_080504	08/05/04	20:30	03:30	CI 18043
Und_090504	09/05/04	20:30	06:30	CI 18043
Und_130504	13/05/04	20:40	03:30	CI 18043
Und_140504	14/05/04	20:30	06:30	CI 18043
Und_160504	16/05/04	22:00	23:53	CI 18043
Und_170504	18/05/04	00:10	05:00	CI 18043
Und_180504	18/05/04	20:30	03:30	CI 18043
Und_190504	19/05/04	21:40	03:40	CI 18027
Und_210504	21/05/04	22:00	06:00	CI 18027

## 3. FRRF Buoy Deployment

File I.D	Start		End		Instrument
	Date	Time	Date	Time	Serial No.
Buoy_1	15/05/04	07:00	17/05/04	11:30	CI 182010
Buoy_2	21/05/04	14:00	22/05/04	13:30	CI 182010

## 4. Optics log

Date	Cast No.	Time	File I.D	Associated CTD Cast	Comments
	1	10:37	2004_127_103749	CTD156_033	Trials
06/05/04	2	11:04	2004_127_110433	CTD156_033	Trials
	3	13:20	2004_127_132051	CTD156_033	Max. Depth 163m
	4	13:30	2004_127_133049	CTD156_033	Max. Depth 163m
	1	12:10	2004_128_121017	CTD156_035	Max. Depth 100m
07/05/04	2	12:20	2004_128_122052	CTD156_035	Max. Depth 120m
	3	12:31	2004_128_123135	CTD156_035	Max. Depth 125m
	1	12:45	2004_129_124514	CTD156_037	Max. Depth 170m
08/05/04	2	12:54	2004_129_125444	CTD156_037	Max. Depth 135m
	3	14:55	2004_129_145531	CTD156_038	Max. Depth 173m
	4	15:09	2004_129_150916	CTD156_038	Max. Depth 165m
	1	11:18	2004_130_111837	CTD156_041	Max. Depth 125m
09/05/04	2	11:27	2004_130_112757	CTD156_041	Max. Depth 127m
	3	11:47	2004_130_114758	CTD156_041	Sky Irradiance
	1	11:11	2004_131_111100	CTD156_042	Max. Depth 108m
10/05/04	2	11:21	2004_131_112101	CTD156_042	Max. Depth 140m

	3	11:31	2004_131_113555	CTD156_042	Sky Irradiance
	1	11:49	2004_132_114935	CTD156_048	Max. Depth 150m
11/05/04	2	11:58	2004_132_115827	CTD156_048	Max. Depth 130m
	3	12:06	2004_132_120645	CTD156_048	Sky Irradiance
	1	13:04	2004_133_130422	CTD156_055	Max. Depth 140m
12/05/04	2	13:18	2004_133_131810	CTD156_055	Max. Depth 130m
	3	13:39	2004_133_133943	CTD156_055	Sky Irradiance
	1	11:10	2004_134_111002	CTD156_056	Sky Irradiance
13/05/04	2	11:28	2004_134_112826	CTD156_056	Max. Depth 122m
	3	11:36	2004_134_113621	CTD156_056	Max. Depth 135m
	1	11:15	2004_135_111540	CTD156_060	Max. Depth 140m
14/05/04	2	11:23	2004_135_112352	CTD156_060	Max. Depth 130m
	3	11:37	2004_135_113750	CTD156_060	Sky Irradiance
	1	13:05	2004_138_130500	CTD156_072	Sky Irradiance
17/05/04	2	13:31	2004_138_133316	CTD156_072	Max. Depth 205m
	3	13:46	2004_138_134611	CTD156_072	Max. Depth 158m
	1	11:19	2004_140_111958	CTD156_075	Max. Depth 182m
19/05/04	2	11:29	2004_140_112910	CTD156_075	Max. Depth 158m
	3	11:43	2004_140_114325	CTD156_075	Sky Irradiance
	4	15:50	2004_140_155053	CTD156_076	Sky Irradiance
	5	16:04	2004_140_160412	CTD156_076	Max. Depth 175m
	1	14:52	2004_141_145226	CTD156_082	Max. Depth 165m
20/05/04	2	15:04	2004_141_150421	CTD156_082	Max. Depth 130m
	3	15:19	2004_141_151952	CTD156_082	Sky Irradiance
21/05/04	1	11:06	2004_142_110630	CTD156_090	Sky Irradiance
	2	11:25	2004_142_112503	CTD156_090	Max. Depth 152m
	1	11:09	2004_143_110924	CTD156_093	Sky Irradiance
22/05/04	2	11:20	2004_143_112036	CTD156_093	
	3	11:32	2004_143_113217	CTD156_093	

5. Filter Log

Date	CTD No.	Analysis	Depth	Volume
				Filtered
			60m	4.22L
		PABS	25m	4.22L
06/05/04	CTD156_033		3m	4.22L
			60m	4.22L
		HPLC	25m	4.22L
			3m	4.22L
			60m	4.22L
		PABS	26m	4.22L
07/05/04	CTD156_035		3m	4.22L
			60m	4.23L
		HPLC	26m	4.23L
			3m	4.24L
			60m	4.22L
08/05/04	CTD156_037	PABS	26m	4.22L
			3m	4.22L
			60m	4.22L
		PABS	26m	4.22L
09/05/04	CTD156_041		3m	4.22L
			60m	4.23L

		HPLC	26m	4.23L
			3m	4.24L
			60m	4.22L
		PABS	26m	4.22L
	CTD156_042		3m	4.22L
			60m	4.23L
10/05/04		HPLC	26m	4.23L
			3m	4.24L
			60m	4.22L
	CTD156_045	PABS	26m	4.22L
			3m	4.22L
			60m	4.22L
12/05/04	CTD156_055	PABS	26m	4.22L
			3m	4.22L
			60m	4.23L
		HPLC	26m	4.23L
			3m	4.24L
		5456	60m	4.22L
13/05/04	CTD156_056	PABS	26m	4.22L
			3m	4.22L
	CTD156 056		60m	4.23L
	C1D130_030	HPLC	26m	4.23L
			3m	4.24L
	CTD156_060	DADC	60m	4.22L
		PABS	20M	4.22L
14/05/04			5111 60m	4.22L
14/03/04		HPLC	26m	4.23L 4.22I
			20111 3m	4.23L 4.24I
	CTD156_061	PARS	26m	4.24L
	010100_001	17100	3m	4.221
	CTD156_072	PABS	60m	4.221
17/05/04			26m	4.221
			3m	4.22L
			60m	4.22L
		PABS	26m	4.22L
	CTD156_075		3m	4.22L
		HPLC	60m	4.23L
19/05/04			26m	4.23L
			3m	4.24L
			60m	4.22L
	CTD156_076	PABS	26m	4.22L
			3m	4.22L
			60m	4.22L
		PABS	26m	4.22L
21/05/04	CTD156_090		3m	4.22L
			60m	4.23L
		HPLC	26m	4.23L
			3m	4.24L
			60m	4.22L
		PABS	26m	4.22L
22/05/04	CTD156_093		3m	4.22L
			60m	4.23L
		HPLC	26m	4.23L
			3m	4.24L

# DISSOLVED IRON DETERMINATION Simon Ussher

#### Aims

- 1. Determine dissolved iron (dFe) ( $<0.2\mu$ m) in the upper water column of fertilised patch areas and outstations and monitor changes in dFe profiles before and after the addition of phosphate/iron.
- 2. Compare any changes in dFe observed with other variables, such as increase of biological activity and vertical transport.
- 3. Determine ultrafiltered ( $<0.02\mu$ m) and dissolved ( $<0.2\mu$ m) iron fractions for selected stations and qualify any temporal changes seen for the small colloidal fraction (i.e.  $0.02 0.2\mu$ m particles).
- 4. Test the suitability of an FI-CL underway dissolved iron analyser for near real time mapping.

### Sampling:

DFe Casts			
Date	Cast	Depths	Comments
28-Apr	003	25, 50, 75, 100, 150, 200	Survey
29-Apr	007	25, 50, 75, 100, 150, 200	Survey
30-Apr	010	25, 50, 75, 100, 150, 200	Survey
1-May	012	25, 50, 75, 100, 150, 200	Survey
2-May	015	25, 50, 75, 100, 150, 200	Survey
3-May	028	25, 50, 75, 100, 150, 200	Phosphate patch
4-May	029	26, 75, 120, 140, 170, 200	Phosphate patch
5-May	030	26, 75, 120, 140, 170, 200	Phosphate patch
6-May	032	26, 75, 120, 140, 170, 200	Phosphate patch
7-May	034	26, 75, 120, 140, 170, 200	Phosphate patch
?	036	26, 75, 120, 140	Phosphate out
8-May	037	26, 75, 120, 140, 170, 200	Phosphate patch
9-May	040	26, 75, 120, 140, 170, 200	Phosphate patch
	042	26, 75, 120	Phosphate out
10-May	043	26, 50, 75, 120	Phosphate patch
11-May	048	26, 50, 75, 120	Phosphate patch -transect
	049	26, 50, 75, 120	Phosphate patch -transect
	050	26, 50, 75, 120	Phosphate patch -transect
	051	26, 50, 75, 120	Phosphate patch -transect
	052	26, 50, 75, 120	Phosphate patch -transect
13-May	057	26, 75, 120, 140, 170, 200	Phosphate patch
14-May	059	26, 75, 120, 140, 170, 200	Phosphate patch
18-May	072	26, 40, 80, 110, 150, 200	Iron Phosphate patch
19-May	074	26, 40, 80, 110, 150, 200	Iron Phosphate patch
	076	26, 40, 110	Iron Phosphate out
20-May	078	26	Iron Phosphate patch -diurnal
	080	26, 40, 80, 110, 150, 200	Iron Phosphate patch -diurnal
	082	26	Iron Phosphate patch -diurnal
	083	26	Iron Phosphate patch -diurnal
	085	26	Iron Phosphate patch -diurnal
21-May	090	26, 40, 110	Iron Phosphate patch
22-May	091	26, 40, 80, 110, 150, 200	Iron Phosphate patch out
23-May	7a.m	26, 40, 80, 110, 150, 200	Iron Phosphate patch

#### -6m depth at 8 knots **SURFACE TOWS Comments** Date 28-29/04/04 overnight hourly data only -survey 30/04 - 01/05/04 overnight hourly data only -survey 01-02/05/04 overnight hourly data only -survey 02-03/05/04 overnight hourly data only -phosphate patch overnight hourly data only -phosphate patch 03/05/04 overnight hourly data only -phosphate patch 05-06/05/04 overnight hourly data only -phosphate patch 07-08/05/04 18-19/05/04 overnight hourly and near real time data -Fe/PO4 patch

## Observations

19-20/05/04

21-22/05/04

1. Dissolved iron (dFe) ( $<0.2\mu$ m) in the upper water column (0 - 200m) of the phosphate fertilised patch (Patch 1), varied from <0.2 - 0.4 nM. The majority of the iron species determined were  $<0.02 \mu$ m in size.

overnight hourly and near real time data -Fe/PO4 patch

overnight hourly and near real time data -Fe/PO4 patch

- 2. A temporal decrease in concentration was seen in the upper water column of the patch 1 while the site was occupied. However, no significant variation was observed between the in and out stations but high biological activity was observed in this area (see James's FRF data).
- 3. In the second patch, where iron was added, dFe concentrations in the mixed layer were raised to  $\sim 0.6$ -1.2 nM after 48 h equilibration and decreased to  $\sim 0.4 0.7$  after  $\sim 72$  h. Further sample and data analysis are required at the home laboratory for more detail of the temporal and spatial variation of this patch.
- 4. The FI-CL underway analyser was tested for near real time mapping of dissolved iron and the results will be correlated with those of discrete samples to check the validity of the data obtained.

...some example data is shown below for patch 1...
# EXAMPLE DATA FOR PATCH 1





#### MICRO AND NANO NUTRIENTS ANALYSIS Malcolm Woodward & Carolyn Harris Objectives:

To investigate the effects on the natural nutrient regimes by the addition of bulk quantities of phosphate compound to the oceanic surface waters, using SF6 as a tracer for the added phosphate patch. Prior to the addition and afterwards to investigate the spatial and temporal variations of the micro nutrients Nitrate, Nitrite, Phosphate, Silicate, and the nanomolar water column variations of Nitrate, Nitrite, Phosphate and Ammonium. The changes over time of the water column nutrients were studied in collaboration with other chemical and biological studies.

# Analytical methodology:

The main nutrient analyser was a 5 channel Bran and Luebbe AAIII, segmented flow autoanalyser. The analytical chemical methodologies were based on the following: Nitrate, (Brewer and Riley, 1965); Nitrite, (Grasshoff, 1976); Phosphate (Kirkwood, 1989); Silicate (Kirkwood, 1989), and Ammonium (Mantoura and Woodward, 1983). All summarised in Woodward (1994). For nanomolar detection limit we deployed an ammonium analytical system which is an adaptation from Jones, 1991. This technique uses a fluorescent analysis technique following ammonia gas diffusion out of the samples, the ammonia passes across a hydrophobic teflon membrane due to pH differential chemistry. This cruise there was also deployed a unique three-channel nanomolar analyser for nitrate, nitrite and phosphate, combining the sensitive segmented flow colorimetric analytical techniques with a Liquid Waveguide Capillary Cell (LWCC). Water samples were taken from the 24 x 10 litre CTD/Rosette system (SeaBird), these were sub sampled into acid clean 60 mls HDPE (nalgene) sample bottles and analysis for the nutrient samples was in most cases complete within 3-4 hours of sampling. Clean handling techniques were employed to avoid any contamination of the samples, particularly for the nanomolar nutrients. No samples were stored.

# **CTD's analysed**

CTD	DATE	<b>PROVISIONAL BOTTLE DEPTHS</b>
CTD004	28.4.04	3, 10, 25, 50, 75, 100, 120, 130, 140, 150, 160, 180, 200, 300
CTD006	29. 4.04	3, 10, 25, 50, 75, 100, 105, 110, 120, 130, 150, 160, 180, 200, 300
CTD 008	29. 4.04	3, 10, 25, 50, 75, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 200, 300
CTD 010	30.4.04	3, 10, 25, 50, 60, 75, 100, 110, 115, 120, 130, 140, 150, 170, 180, 190, 200, 300
CTD 012	1.5.04	5, 10, 25, 50, 75, 100, 105, 110, 115, 120, 130, 140, 150, 160, 170, 180, 200, 300
CTD 013	1.5.04	5, 10, 25, 50, 75, 100, 110, 115, 120, 125, 130, 135, 140, 150, 160, 180, 200, 300
CTD 028	3.5.04	3, 10, 25, 40, 50, 60, 75, 100, 120, 130, 135, 140, 160, 170, 180, 200, 300
CTD 029	4.5.04	3, 10, 15, 26, 40, 60, 65, 75, 100, 111, 120, 140, 150, 160, 170, 200, 300
CTD 030	5.5.04	3, 10, 15, 26, 40, 50, 60, 80, 100, 115, 130, 150, 160, 180, 200
CTD 032	6.5.04	3, 10, 15, 26, 40, 50, 60, 70, 80, 100, 110, 120, 140, 150, 160, 180, 200
CTD 034	7.5.04	3, 10, 15, 26, 40, 50, 60, 70, 80, 100, 120, 130, 140, 150, 160, 180, 200,
CTD 035	7.5.04	3, 10, 15, 26, 40, 50, 60, 70, 80
CTD 036	7.5.04	3, 10, 15, 26, 40, 50, 60, 70, 80, 100, 110, 120, 130, 140, 150, 160, 180, 200,
CTD 037	8.5.04	3, 10, 15, 26, 40, 50, 60, 70, 80, 100, 120, 130, 150, 170, 200
CTD 038	8.5.04	3, 10, 15, 26, 40, 50, 60, 70, 100, 125, 135, 160, 180, 200,
CTD 040	9.5.04	3, 10, 26, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 100, 120, 170, 200,
CTD 042	9.5.04	3, 10, 26, 40, 50, 60, 70, 80, 100, 120, 130, 150, 160, 180, 200,
CTD 043	10.5.04	3, 10, 15, 26, 40, 50, 55, 60, 65, 70, 75, 80, 100, 120, 150, 170, 200,
CTD 054	12.5.04	3, 10, 26, 40, 50, 60, 70, 75, 80, 90, 100, 120, 140, 160, 180, 200,
CTD 057	13.5.04	3, 10, 26, 40, 60, 70, 75, 80, 85, 90, 100, 135, 150, 180, 200,
CTD 059	14.5.04	3, 10, 26, 40, 60, 70, 80, 85, 90, 95, 100, 120, 150, 180, 200
CTD 061	14.5.04	3, 10, 26, 40, 60, 75, 100, 120, 130, 140, 160, 180, 200,

CTD 062	15.5.04	3, 10, 26, 40, 60, 80, 85, 90, 95, 100, 130, 150, 170, 200,
CTD 069	16.5.04	3, 10, 26, 40, 60, 70, 80, 100, 110, 120, 130, 140, 150, 160, 180, 200
CTD 071	17.5.04	3, 10, 26, 30, 40, 60, 80, 90, 100, 120, 130, 140, 160, 180, 200,
CTD 072	17.5.04	3, 10, 26, 40, 60, 80, 90, 100, 110, 115, 120, 140, 160, 180, 200,
CTD 074	19.5.04	3, 10, 20, 26, 30, 40, 50, 60, 80, 100, 110, 120, 140, 180, 200,
CTD 076	19.5.04	3, 10, 26, 40, 60, 80, 100, 105, 110, 115, 120, 140, 160, 180, 200,
CTD 077	19.5.04	100, 200, 300, 400, 500, 600, 700, 800, 900, 1000
CTD 080	20.5.04	3, 10, 20, 26, 30, 35, 40, 45, 50, 60, 80, 100, 120, 140, 160, 200,
CTD 089	21.5.04	3, 10, 20, 26, 30, 35, 40, 60, 80, 100, 110, 120, 140, 160, 200,
CTD 090	21.5.04	3, 20, 26, 30, 35, 40, 50, 60, 80, 100, 120, 140, 160, 200,
CTD 092	22.5.04	3, 10, 15, 20, 26, 30, 35, 40, 45, 60, 80, 100, 110, 120, 150, 200,
CTD 093	22.5.04	3, 10, 26, 40, 60, 80, 100

2) CTD Analysis for nanomolar Ammonium concentrations by the Teflon membrane/fluorescence technique.

CTD	DATE	PROVISIONAL BOTTLE DEPTHS
CTD004	28.4.04	3, 10, 25, 50, 75, 100, 120, 130, 140, 150, 160, 200, 300
CTD006	29. 4.04	3, 10, 25, 50, 75, 100, 105, 110, 150, 180, 200, 300
CTD 010	30.4.04	3, 10, 25, 50, 75, 100, 110, 115, 120, 130, 140, 150, 200, 300
CTD 012	1.5.04	5, 10, 25, 50, 100, 105, 110, 115, 120, 130, 140, 160, 200, 300
CTD 013	1.5.04	5, 10, 25, 50, 100, 110, 115, 120, 125, 130, 160, 300
CTD 028	3.5.04	3, 10, 25, 50, 75, 100, 130, 135, 140, 160, 180, 300
CTD 029	4.5.04	3, 10, 15, 26, 60, 65, 75, 100, 111, 120, 140, 150, 160, 170, 200, 300
CTD 030	5.5.04	3, 10, 15, 26, 50, 60, 100, 115, 130, 160,
CTD 032	6.5.04	10, 15, 26, 40, 50, 60, 70, 80, 100, 110, 120, 140, 150, 200
CTD 034	7.5.04	10, 15, 26, 40, 50, 60, 70, 80, 100, 120, 150, 200,
CTD 036	7.5.04	3, 10, 15, 26, 40, 50, 80, 100, 110, 120, 150, 200,
CTD 037	8.5.04	3, 10, 15, 26, 40, 50, 60, 80, 100, 120, 130, 150, 170, 200
CTD 038	8.5.04	3, 10, 15, 26, 40, 50, 60, 70, 100, 125, 135, 160, 180, 200,
CTD 040	9.5.04	3, 10, 26, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 100, 120, 170, 200,
CTD 042	9.5.04	3, 10, 26, 40, 50, 60, 100, 120, 130, 160, 180, 200,
CTD 043	10.5.04	3, 10, 15, 26, 40, 50, 55, 60, 65, 70, 75, 80, 100, 120, 150, 170, 200,
CTD 046	11.5.04	3, 10, 26, 40, 50, 55, 60, 65, 70, 80, 100
CTD 047	11.5.04	3, 10, 26, 40, 50, 60, 65, 70, 80, 85, 100
CTD 048	11.5.04	3, 10, 26, 40, 50, 60, 65, 70, 80, 85, 100
CTD 049	11.5.04	3, 10, 26, 40, 50, 60, 65, 70, 75, 80, 100
CTD 050	11.5.04	3, 10, 26, 40, 50, 60, 65, 70, 75, 80, 100
CTD 051	11.5.04	3, 10, 26, 40, 50, 60, 65, 70, 75, 80, 100
CTD 054	12.5.04	3, 10, 26, 40, 50, 60, 70, 75, 80, 90, 100, 120, 140, 160, 180, 200,
CTD 057	13.5.04	3, 10, 26, 40, 60, 70, 75, 80, 85, 90, 100, 135, 150, 180, 200,
CTD 059	14.5.04	3, 10, 26, 40, 60, 70, 80, 85, 90, 95, 100, 120, 150, 180, 200
CTD 061	14.5.04	3, 10, 26, 40, 60, 75, 100, 120, 130, 140, 160, 180, 200,
CTD 062	15.5.04	3, 10, 26, 40, 60, 80, 85, 90, 95, 100, 130, 150, 170, 200,
CTD 069	16.5.04	3, 10, 26, 40, 60, 70, 80, 100, 110, 120, 130, 140, 150, 160, 180, 200
CTD 071	17.5.04	3, 10, 26, 30, 40, 60, 80, 90, 100, 120, 130, 140, 160, 180, 200,
CTD 072	17.5.04	3, 10, 26, 40, 60, 80, 90, 100, 110, 115, 120, 140, 200,
CTD 074	19.5.04	3, 10, 20, 26, 30, 40, 50, 60, 80, 100, 110, 120, 140, 180, 200,
CTD 076	19.5.04	3, 10, 26, 40, 60, 80, 100, 105, 110
CTD 080	20.5.04	3, 10, 20, 26, 30, 35, 40, 45, 50, 60, 80, 100, 120, 140, 160, 200
CTD 089	21.5.04	3, 10, 20, 26, 30, 35, 40, 60, 80, 100, 110, 120, 140, 160
CTD 090	21.5.04	3, 20, 26, 30, 35, 40, 50, 60, 80, 100, 120, 140, 160, 200
CTD 092	22.5.04	3, 10, 15, 20, 26, 30, 35, 40, 45, 60, 80, 100, 110, 120, 150, 200
CTD 093	22.5.04	3, 10, 26, 40, 60, 80, 100

CTD	DATE	DDOVISIONAL ROTTLE DEDTUS
	29 4 04	2 10 25 50 75 100 120 120 140 150 160 100 200
CTD004	20.4.04	3, 10, 25, 50, 75, 100, 120, 130, 140, 130, 160, 180, 200, 300
CTD 008	20.4.04	3 10 25 50 75 90 100 110 120 130 140 150 160 170 180 200 300
CTD 000	20.4.04	3 10 25 50 60 75 100 110 115 120 130 140 150 170 180 100 200 300
CTD 010	1 5 04	5, 10, 25, 50, 60, 75, 100, 115, 110, 115, 120, 130, 140, 150, 170, 160, 130, 200, 300
CTD 012	1.5.04	5, 10, 25, 50, 75, 100, 110, 115, 120, 125, 130, 135, 140, 150, 160, 170, 160, 200, 300
CTD 010	3.5.04	3, 10, 25, 40, 50, 60, 75, 100, 120, 130, 135, 140, 160, 170, 180, 200, 300
CTD 029	4.5.04	3. 10. 15. 26. 40. 60. 65. 75. 100. 111. 120. 140. 150. 160. 170. 200. 300
CTD 030	5.5.04	3, 10, 15, 26, 40, 50, 60, 80, 100, 115, 130, 150, 160, 180, 200
CTD 032	6.5.04	3, 10, 15, 26, 40, 50, 60, 70, 80, 100, 110, 120, 140, 150, 160, 180, 200
CTD 034	7.5.04	3, 10, 15, 26, 40, 50, 60, 70, 80, 100, 120, 130, 140, 150, 160, 180, 200,
CTD 035	7.5.04	3, 10, 15, 26, 40, 50, 60, 70, 80
CTD 036	7.5.04	3, 10, 15, 26, 40, 50, 60, 70, 80, 100, 110, 120, 130, 140, 150, 160, 180, 200,
CTD 037	8.5.04	3, 10, 15, 26, 40, 50, 60, 70, 80, 100, 120, 130, 150, 170, 200
CTD 038	8.5.04	3, 10, 15, 26, 40, 50, 60, 70, 100, 125, 135, 160, 180, 200,
CTD 040	9.5.04	3, 10, 26, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 100, 120, 170, 200,
CTD 042	9.5.04	3, 10, 26, 40, 50, 60, 70, 80, 100, 120, 130, 150, 160, 180, 200,
CTD 043	10.5.04	3, 10, 15, 26, 40, 50, 55, 60, 65, 70, 75, 80, 100, 120, 150, 170, 200,
CTD 046	11.5.04	3, 10, 26, 40, 50, 55, 60, 65, 70, 80, 100
CTD 047	11.5.04	3, 10, 26, 40, 50, 60, 65, 70, 80, 85, 100
CTD 048	11.5.04	3, 10, 26, 40, 50, 60, 65, 70, 80, 85, 100
CTD 049	11.5.04	3, 10, 26, 40, 50, 60, 65, 70, 75, 80, 100
CTD 050	11.5.04	3, 10, 26, 40, 50, 60, 65, 70, 75, 80, 100
CTD 051	11.5.04	3, 10, 26, 40, 50, 60, 65, 70, 75, 80, 100
CTD 054	12.5.04	3, 10, 26, 40, 50, 60, 70, 75, 80, 90, 100, 120, 140, 160, 180, 200,
CTD 057	13.5.04	3, 10, 26, 40, 60, 70, 75, 80, 85, 90, 100, 135, 150, 180, 200,
CTD 059	14.5.04	3, 10, 26, 40, 60, 70, 80, 85, 90, 95, 100, 120, 150, 180, 200
CTD 061	14.5.04	3, 10, 26, 40, 60, 75, 100, 120, 130, 140, 160, 180, 200,
CTD 062	15.5.04	3, 10, 26, 40, 60, 80, 85, 90, 95, 100, 130, 150, 170, 200,
CTD 069	16.5.04	3, 10, 26, 40, 60, 70, 80, 100, 110, 120, 130, 140, 150, 160, 180, 200
CTD 071	17.5.04	3, 10, 26, 30, 40, 60, 80, 90, 100, 120, 130, 140, 160, 180, 200,
CTD 072	17.5.04	3, 10, 26, 40, 60, 80, 90, 100, 110, 115, 120, 140, 160, 180, 200,
CTD 074	19.5.04	3, 10, 20, 26, 30, 40, 50, 60, 80, 100, 110, 120, 140
CTD 075	19.5.04	3, 10, 20, 26, 28, 30
CTD 076	19.5.04	3, 10, 26, 40, 60, 80, 100, 105, 110, 115
CTD 080	20.5.04	3, 10, 20, 26, 30, 35, 40, 45, 50, 60, 80, 100, 120, 140
CTD 089	21.5.04	3, 10, 20, 26, 30, 35, 40, 60, 80, 100, 110, 120, 140
CTD 090	21.5.04	3, 20, 26, 30, 35, 40, 50, 60, 80, 100, 120
CTD 092	22.5.04	3, 10, 15, 20, 26, 30, 35, 40, 45, 60, 80, 100, 110, 120
CTD 093	22.5.04	3, 10, 26, 40, 60, 80, 100

*3)* Nanomolar nutrients analysis for nitrate, nitrite and phosphate by Liquid Waveguide Capillary Cells, following segmented flow colorimetric analysis:

# **Underway Analysis:**

Underway sampling was carried out from the surface (7m) non-toxic sea -water supply for nanomolar phosphate analysis through the waveguide nutrient analyser. This was filtered by 0.45 um Millipore filter prior to analysis:

Times of the underway:

5/504 at 2320 to 6/5/04 at 0402, 6/5/04 at 1334 to 7/5/04 at 0730

7/5/04 at 2130 to 8/5/04 at 0940, 8/5/04 at 2134 to 9/5/04 at 0739

9/5/04 at 2048 to 10/5/04 at 0730, 11/5/04 at 2325 to 12/5/04 at 0628

12/5/04 at 2135 to 13/5/04 at 0600, 13/5/04 at 2135 to 14/5/04 at 0600

14/5/04 at 2014 to 15/5/04 at 0604, 18/5/04 at 1947 to 19/5/04 at 0652

# **Other Analyses:**

Samples were analysed for DOM (DON and DOP), these were the reanalysis after chemical digestion from experiments carried out by Mireille Pujo-Pay and Pascal Conan from the French laboratory at Banyuls -sur-mer.

These analyses in combination with the original nutrient concentrations will allow the reporting of the organic matter content of the waters during the experiment.

1) By 5 channel Bran and Luebbe autoanalyser For Micromolar Nitrate and Phosphate following chemical digestion for DOM: All samples are analysed in duplicate !

CTD	DATE	SAMPLE BOTTLES
CTD004	28.4.04	Rea24,22, 20, 18, 16, 15, 14, 13, 12, 11, 10, 9, 8
CTD 008	29. 4.04	Rea, 24, 20, 18, 15, 14, 13, 12, 11, 10, 9, 8
CTD 010	30.4.04	Rea, 24,22, 21, 20, 18, 13, 8, 7
CTD 012	1.5.04	Rea, 24,23, 22, 20, 19, 17, 16, 15, 14, 13, 11, 8, 7
CTD 013	1.5.04	Rea, 24,22, 20, 18, 16, 15, 14, 13, 12, 11, 10, 9, 8
CTD 028	3.5.04	Rea, bio, 24,22, 20, 17, 16, 15, 13, 12, 11, 10, 7
CTD 029	4.5.04	Rea, bio, 24,22, 19, 18, 16, 15, 14, 13, 12, 10, 8, 7
CTD 030	5.5.04	Rea, bio3, bio1, bio4, bio1, bio2, 24,22, 21, 19, 17, 16, 15, 14, 13, 12, 10, 7
CTD 032	6.5.04	Rea, biop,. Bio, 24,22, 21, 20, 19, 17, 15, 14, 13, 12, 11, 9, 7
CTD 034	7.5.04	Rea, 24,21, 20, 19, 17, 15, 14, 13, 12, 11, 9, 7
CTD 036	7.5.04	Rea, 24,22, 21, 19, 16, 15, 14, 13, 12, 11, 9, 7
CTD 037	8.5.04	Rea, bio1, bio2, bio3, bio4, 24,21, 20, 17, 13, 12, 11, 10, 9, 7
CTD 040	9.5.04	Rea, bio, bio, bio, 24,21, 20, 19, 17, 15, 13, 11, 10, 9, 8, 7
CTD 042	9.5.04	Rea, 24,22, 20, 19, 18, 15, 13, 12, 11, 10, 8, 7
CTD 062	15.5.04	Rea, 24,22, 20, 18, 17, 16,14, 12, 10, 9, 8, 7
CTD 069	16.5.04	Tank1, tank2, tank3, tank4, tank5, rea, 24,22, 20, 18, 16, 15, 13, 12, 11, 10, 8, 7
CTD 071	17.5.04	Rea, 24,22, 20, 18, 16, 15, 13, 12, 11, 10, 9, 7
CTD 069	16.5.04	rea, 24,22, 20, 18, 16, 14, 13, 12, 11, 10, 8,
CTD 071	17.5.04	Rea, 24,22, 20, 18, 16, 15, 13, 12, 11, 10, 9
CTD 074	19.5.04	Rea, 24,22, 20, 17, 14, 13, 12, 11, 10, 9, 8, 7
CTD 075	19.5.04	REA, 24, 2, 21, 20, 17
CTD 076	19.5.04	Rea, 24,22, 21, 19, 18, 16, 15, 13, 10
CTD 079	20.5.04	REA, 24,22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8
CTD 080	20.5.04	Rea, 24,22, 21, 18, 17, 16, 14, 12, 11, 10, 9, 7
CTD 089	21.5.04	Rea, 24,22, 21, 20, 18, 13, 12, 11, 10, 9, 7
CTD 092	22.5.04	Rea, 24,22, 21, 20, 17, 15, 13, 11, 10, 9, 8, 7
CTD 093	22.5.04	Rea, 24,22, 20, 19, 16, 15, 12

Also, approximately 30 samples for nanomolar ammonium analyses from an on-deck ammonium photoproduction experiment that was attempted.

# **Preliminary Results**

Surface nanomolar concentrations prior to the 'seeding' of he patch area with phosphate were less than 10 nanomoles of phosphate, less than 5 nanomoles of nitrate and less than 1 nanomole of nitrite. Following the addition of the phosphate the surface concentrations increased to over 120 nanomoles at the centre of the patch. During the first experiment this decreased during the study period of about 8 days and was found as deep as 90 metres by the end of the study. This co-incided with the SF6 traces which also was found getting deeper during the experiment. The surface mapping showed excellent correlations between the phosphate and the SF6. Plotting the SF6 and the phosphate over the time period it appeared to demonstrate that their was little uptake of the phosphate with the main reason for the lowered surface concentrations being dilution to depth.

# MEASUREMENTS OF DISSOLVED AND PARTICULATE CARBON, NITROGEN AND PHOSPHORUS: BIODEGRADATION OF DISSOLVED ORGANIC MATTER *Mireille Pujo-Pay and Pascal Conan*

#### **Studied parameters** *Vertical DOM profiles*

During the FEEP cruise, vertical profiles of dissolved organic carbon (DOC), nitrogen and phosphorus (DON and DOP) as well as particulate nitrogen and phosphorus (PN and PP) have been determined from samples collected from CTD cast in and out of the patch (see table below). Some analyses have been performed during the cruise while some will be done when return to the laboratory in Banyuls (especially for particulate matter and DOC, see details below). The different profiles out of the patch will allow us to determine the time and space scale of the eventual variability in DOM distribution in the area of study. The profiles in the patch will allow us to see the influence of the enrichment on the studied parameters.

### Lability of DOM

DOC dynamics and export are important factors in the fate and removal of organic carbon from pelagic ecosystems. However, usually the relative importance depends largely on the production and consumption processes of the system. In the case production and consumption are tightly coupled, little freshly produced labile is then available for export. During the FEEP cruise, we wanted to see the influence of the different enrichments in the surface waters of the tropical Atlantic on the *in situ* biological processes. During the last decade, there has been a renewed interest in the study of the effects of light radiations in aquatic environments, induced by a potential increase of UV (Ultra-Violet radiations) flux related to the diminution of the stratospheric ozone concentration. Results show that numerous biological and chemical processes can be affected by UV radiations, even at a "common level" (see for example Hader et al., 1998). Consequently, UV radiations should be considered as a natural abiotic factor and their impacts studied in the same way as PAR, temperature or nutrient availability. It is now well recognized that the UV radiations have contradictory effects on biological and chemical components of the ecosystems. They might both stimulate and/or suppress bacterial activity and phytoplankton photosynthesis through the direct impact or indirect via Dissolved Organic Matter (Gustavson et. al., 2000; Eilertsen and Holm-Hansen 2000). This suggests drastic variations in the ratio of bacterial production to primary production and in the f-ratios, which in terms are directly related to the export of matter towards the deep ocean.

To access the bio-availability of DOM during the FEEP cruise, biodegradation experiments of dissolved organic matter have been carried out. The influence of the combined role of PO4 enrichment and light (especially UV radiations) on the lability of DOM have been estimated through bacterial utilisation of DOM during 5 biodegradation experiments. This experimental work will give a dynamic view of the system and allow to check if the behaviour of DOM is conservative or if the chemical environment can have a significant importance on biology and successively on DOM fluxes through the microbial food web.

#### Incubation experiment on the Poseidon

During incubation experiments carried out on the Poseidon by Carol Robinson, samples for DOC have been collected and stored. They will be analysed when return to the laboratory in Banyuls (see Carol Robinson for experimental details). During incubation experiments carried out on the Poseidon by Andy Rees (5 tanks under different enrichment conditions), samples for dissolved organic matter have been collected. Samples for DOC have been stored and will be analysed when return to the laboratory as samples for DON and DOP have been analysed on board (transfer of samples on the C. Darwin) (see Andy Rees for experimental details of the incubations).

### Methods and number of samples

#### Dissolved organic carbon - DOC

Samples for DOC measurements have been be filtered through 2 pre-combusted glass fiber Whatman GF/F filters, poisoned with mercury chloride (5 mg/l) and stored in glass tubes. Further analysis of the dissolved organic carbon (DOC) will be performed when return to the laboratory using a high temperature catalytic oxidation (HTCO) technique (Sugimura & Suzuki, 1988), reviewed by Cauwet (1994) with a Shimadzu TOC V. 23 profiles (524 measures including replicates) of DOC will be obtained "in and out" of the different patch enrichments.

### Dissolved organic nitrogen and phosphorus (DON and DOP)

Duplicate samples for DON and DOP have been analysed during the cruise by the wet oxidation procedure (Pujo-Pay & Raimbault, 1994 and Pujo-Pay et al 1997). A triplicate sample has been collected and will be analysed when return to the laboratory in Banyuls. 24 profiles (825 measures including triplicates) will be obtained "in and out" of the different patch enrichments. Further analyses have been performed for nanomolar determination of DOP. The exploitations of these results will be done when return to the laboratory.

### Particulate nitrogen and phosphorus (PN and PP)

Samples for analyses of Particulate nitrogen and phosphorus have been filtered and store until further analyses when return to the laboratory. Analyses will be performed by the wet oxidation procedure of Pujo-Pay & Raimbault (1994). 23 profiles (490 measures including some duplicates) will be obtained "in and out" of the patch enrichments.

### **Biodegradation experiments**

5 Biodegradation experiments have been carried out during the cruise. Time-series sampling for DOC, DON and DOP have been done during the cruise and will been continued when return to the laboratory.

Controls:

Bio 1 : control biodegradation – out of the patch at 120m deep (just before the chlorophyll maximum)

Bio 2 : control biodegradation – out of the patch at 40m deep (in the max of bacterial biomass)

Influence of in situ PO4 enrichment

Bio3 : in the patch after enrichment of PO4 at 40m deep

# Influence of UV Radiation

Bio4 : in the patch after enrichment of PO4 at 40m deep and after DOM have been exposed two days to solar radiations.

Influence of PO4 +NO3+NH4 enrichments

Bio3 : out the patch with experimental enrichments of PO4, NO3 and NH4 (N/P~4) at 40m deep

	number of donth analysed					
	T	CTTD	Data	DOC		
	1	CID	Date	DOC	DON & DOP	PN & PP
survey		IM2	28/04/2004		14	11
		IM5	29/04/2004		9	9
		IM9	01/05/2004	13	13	12
		IM025	03/05/2004	11	11	
Patch 1 + PO4						
out	Т0	029	04/05/2004	12	12	11
in	T1	030	05/05/2004	12	12	12
in	T2	032	06/05/2004	12	12	12
in	T5	034	07/05/2004	12	12	12
out	T7	036	07/05/2004	12	12	11
in	T8	037	08/05/2004	10	10	10
in	T11	040	09/05/2005	12	12	6
out	T13	042	09/05/2004	12	12	12
in	T33	062	15/05/2005	14	13	13
Patch 2 Fe+PO4	4					
out	<b>TB00</b>	069	16/05/2004	12	12	12
In (+Fe)	TB02	071	17/05/2004	12	12	12
In (+Fe)	<b>TB03</b>	072	17/05/2004	12	12	12
in ( +PO4)	<b>TB05</b>	074	19/05/2004	12	12	12
in)	<b>TB06</b>	075	19/05/2005	5	5	5
out	<b>TB07</b>	076	19/05/2005	9	9	9
out deep	ST08	077	19/05/2004	16	16	-
in	Diel 03	080	20/05/2004	12	12	12
in	<b>TB09</b>	089	21/05/2004	12	12	12
out	TB011	091	21/05/2004	9	-	9
in	TB012	092	22/05/2004	12	12	12
out	TB13	093	22/05/2004	7	7	7

#### Measurements during the CTD cast (profiles)

#### References

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#### PHYTOPLANKTON COMMUNITY STRUCTURE AND ABUNDANCE BY FLOW CYTOMETRY AND MICROSCOPY *Glen Tarran*

# Introduction

The oligotrophic ocean is numerically dominated by bacteria and viruses. Whilst very little is currently known about viruses; bacteria, both heterotrophic and autotrophic are very important components of the microbial foodweb in these waters, with autotrophic cyanobacteria often contributing >50% to primary production in surface waters. Recent bottle incubation experiments in which oligotrophic seawater was incubated over 24-48 h with combinations of added iron, nitrogen and/or phosphorous have shown a cascade effect of increasing nitrogen fixation, primary production and picophytoplankton abundance with more complex combinations of added nutrients. The FeEPO4 cruise provided the opportunity to test some of the nutrient combinations (phosphorous alone (as phosphate) and phosphorous and iron (as ferrous sulphate) together), in the field through the addition of nutrients directly to areas of the ocean that were then traced using sulphurhexafluoride, added with the nutrients.

To study any changes in the planktonic communities in the different patches, a combination of flow cytometric analysis of live samples and collection of preserved samples for postcruise analysis was carried out during the cruise to quantify viruses, heterotrophic bacteria, autotrophic cyanobacteria, pico and nano eukaryote phytoplankton and microplankton

# Studies undertaken

- 1) Analysis of fresh seawater samples to determine the temporal abundance and community structure of nano and picoplankton in surface waters at CTD stations by flow cytometry.
- **2)** Collection of preserved seawater samples (Lugol's iodine) (for Claire Widdicombe) for analysis of nano and microplankton abundance and community structure in surface waters at CTD stations by microscopy.
- **3)** Collection of preserved seawater samples for the post-cruise quantification of heterotrophic bacteria and viruses through the water column at CTD stations by flow cytometry.
- **4)** Analysis of live samples from dilution grazing experiments to determine autotrophic cyanobacterial abundance; with Susan Kimmance and Stephen Archer. (See Susan's cuise report for details).

# Methods

Fresh seawater samples were collected in clean 250 mL polycarbonate bottles from a Seabird CTD system containing 24 x 10 L Trace Metal Niskin bottles from CTD casts. Samples were stored in a refrigerator until analysed (less than 2 hours). 2 mL samples were used for immediate flow cytometric analysis to characterise and enumerate prochlorophytes, cyanobacteria, pico-eukaryotes and nanophytoplankton based on their light scattering and fluorescence properties. The flow cytometer used was a Becton Dickinson FACSort instrument. Of the 2 mL, approx 300µl of sample was actually analysed to provide vertical profiles of phytoplankton abundance per millilitre, generally down to 200 m. Samples from the same depths were also preserved immediately for analysis of bacterial and virus abundance back in the laboratory. Samples for viral analysis were preserved with glutaraldehyde (0.5% final) for 30 mins at 4°C, flash frozen in liquid nitrogen for 50 s and stored at -80°C. Samples for bacterial analysis were preserved with paraformaldehyde (1% final) at 4°C for 24 h and then stored at -80°C. Additional 500 mL samples were also taken from 6 selected depths down to the chlorophyll maximum and preserved with Lugol's iodine. Table 1 summarises the CTD casts sampled and analysed during the cruise.

Table 1: CTD casts sampled for plankton community structure

DATE	CTD	RSU#	TIME (GMT)	LAT N	LONG W	DEPTH RANGE SAMPLED
28-Apr	IM1	CD156 003	7:53	27.36	22.69	6-150m
28-Apr	IM2	CD156_004	15:03	27.97	23.44	3-150m
29-Apr	IM3	CD156_006	5:01	26.75	23.47	6-150m
29-Apr	IM4	CD156_007	15:03	27.97	23.44	3-150m
29-Apr	IM5	CD156_008	19:30	26.14	23.40	3-150m
30-Apr	IM6	CD156_009	1:24	25.60	23.98	3-150m
30-Apr	IM7	CD156_010	9:40	24.82	24.82	3-150m
1-May	IM9	CD156_012	10:55	27.81	25.02	3-150m
1-May	IM10	CD156_013	18:48	28.42	24.37	3-150m
2-May	IM12	CD156_015	9:23	27.90	23.51	3-150m
4-May	ТО	CD156 029	10:06	27.41	23.33	3-200m
5-May	T1IN	CD156_030	20:10	27.79	23.31	3-200m
6-May	T3IN	CD156_032	8:16	27.76	23.28	3-200m
7-May	T5IN	CD156_034	8:45	27.72	23.22	3-200m
7-May	T5IN	CD156_035	14:17	27.73	23.22	2-80m
7-May	T7OUT	CD156_036	16:51	27.74	23.35	3-200m
8-May	T8IN	CD156_037	12:24	27.68	23.24	3-200m
8-May	T9OUT	CD156_038	16:40	27.69	23.05	3-200m
9-May	T11IN	CD156_040	8:42	27.69	23.23	3-200m
9-May	T13OUT	CD156_042	16:17	27.79	23.23	3-200m
1-May	T14IN	CD156_043	8:40	27.66	23.22	3-200m
10-Mav	T16OUT	CD156_045	15:57	27.55	23.35	3-200m
11-Mav	T17T1	CD156 046	6:58	27.66	23.35	3-60m
11-Mav	T18T1	CD156_047	8:50	27.71	23.30	3-80m
11-Mav	T19T1	CD156 048	10:56	27.69	23.33	3-80m
11-Mav	T20T1	CD156 049	12:59	27.68	23.34	3-80m
11-Mav	T21T1	CD156 050	14:59	27.66	23.36	3-80m
11-May	T22T1	CD156 051	19:21	27.65	23.37	3-80m
11-May	T23T1	CD156_052	21:24	27.62	23.41	3-80m
12-May	T25IN	CD156_054	8:04	27.66	23.37	3-200m
13-May	T28IN	CD156_057	17:25	27.75	23.40	3-200m
14-May	T30IN	CD156_059	8:32	27.62	23.27	3-200m
14-May	T32OUT	CD156_061	15:45	27.69	23.19	3-200m
15-May	T33IN	CD156_062	8:26	27.62	23.24	3-200m
16-May	<b>TB00</b>	CD156 069	5:38	27.54	22.57	3-200m
17-May	TB02IN	CD156_071	8:07	27.55	23.54	3-200m
17-May	TB03IN	CD156_072	15:00	27.57	22.46	3-200m
19-May	TB05IN	CD156_074	8:30	27.66	22.31	3-200m
19-May	TB07OUT	CD156_076	15:44	27.67	22.38	3-200m
20-May	DIEL3IN	CD156_080	9:06	27.64	22.25	3-200m
20-May	DIEL5IN	CD156_082	14:35	27.68	22.22	3-150m
20-May	DIEL6IN	CD156_083	16:48	27.68	22.21	3-150m
20-May	DIEL8IN	CD156_085	20:36	27.68	22.21	3-150m
21-May	TB09IN	CD156_089	8:05	27.67	22.21	3-200m
21-May	TB11OUT	CD156_091	16:50	27.69	22.28	3-200m
22-May	TB12IN	CD156_092	8:16	27.70	22.06	3-200m
22-May	TB13OUT	CD156_093	12:08	27.79	22.05	3-200m

#### PHYTOPLANKTON PIGMENT ANALYSIS Alexandre B. de Menezes Background

# Background

Samples were taken for the future analysis of phytoplankton pigments using HPLC (High Performance Liquid Chromatography). HPLC is an accurate technique that allows for the precise separation, identification and quantification of phytoplankton pigments. The pigments, such as chlorophyll a and divinyl chlorophyll a are used to measure phytoplankton biomass in the water column and also can be used as biomarkers of specific micro-algae groups such as the cyanobacteria and diatoms, giving insights into phytoplankton community structure and its dynamics.

# **Purpose of analysis**

In this cruise, the pigment analysis will give a measure of biomass of the total population and of different phytoplankton groups and also reveal changes occurring with the phytoplankton population during the experiments, whether there was an increase or a decrease in total biomass and whether there was a relative change in the contribution of different algal groups to the phytoplankton community.

### Methods

The samples were obtained by vacuum filtration of water into glass fiber filters that were flash freezed and stored in liquid nitrogen. Between 2.10 and 4.6 liters of water were filtered. Between 6 to 10 different depths were sampled throughout the water column up to 200 meters to include the deep chlorophyll maximum, the mixed layer and the depths where the nutrients were to be released. Samples were taken before the nutrient addition to characterize the phytoplankton population prior to the experiment and, after the addition, samples were taken generally twice a day, one from "inside patch" stations in the morning CTD cast and another from "out of patch" stations in the afternoon. Samples were also taken during the transect through the phosphate patch and from the diel experiment. Two non toxic samples were taken per day.

Date	CTD	Depth	Volume (Liters)
28/04/04	CTD 4	300	2.112
		200	2.110
		150	2.112
		120	2.117
		100	2.111
		75	2.111
		50	2.114
		25	2.128
		10	2.126
		3	2.130
29/04/04	CTD 6	300	2.112
		200	2.110
		180	2.112
		160	2.117
		150	2.111
		130	2.111
		100	2.114
		50	2.128
		10	2.126
		3	2.130
	CTD 7	200	2.112
		180	2.110

Table 1 – samples taken during CD 156 FeeP cruise

		150	2.112
		120	2.117
		100	2.111
		75	2.111
		50	2.114
		25	2.128
		10	2.126
		3	2.130
	CTD 8	200	2.111
		150	2.111
		100	2.114
		50	2.128
		25	2.126
		3	2.130
	CTD 9	150	2.112
		125	2.117
		100	2.111
		75	2.111
		50	2.114
		30	2.128
		15	2.126
		3	2.130
30/04/04	CTD 10	180	2.112
		130	2.110
		100	2.112
		50	2.117
		25	2.111
		3	2.111
01/05/04	CTD 12	200	2.112
		150	2.110
		130	2.112
		110	2.117
		50	2.111
		25	2.111
		10	2.114
02/05/04	CTD 15	180	2.112
		150	2.110
		110	2.112
		75	2.117
		50	2.111
		24	2.111
02/05/04		3	2.114
03/03/04	C1D 28	200	2.112
		160	2.110
		130	2.112
		100	2.117
		30	2.111 9.111
		20	2.111
04/05/04	CTD 20	3 170	2.114
UT/UJ/UH	T0 - phosphate addition	150	2 110
		111	9 119
		75	».116 9 117
		65	2 111
		40	2 111
		26	2 114
		w V	W.111

		15	2.128
		10	2.126
		3	2.130
05/04/04	CTD 30	150	2.112
	T1 – phosphate addition	130	2 110
	in patch station	115	2 112
	r	80	2 117
		50	2 111
		40	2 111
		26	2 114
		15	2 128
		10	2 126
		3	2 130
06/05/04	CTD 32	150	2 112
00/03/04	in patch station	140	2.112
	in paten station	140	2.110
		80	2.112
		50	9 111
		<u> </u>	2.111
		40	2.111
		15	2.114
		10	2.120
		10	2.120
07/05/04	CTD 34	150	2.130
07/03/04	In patch station	130	2.112
	in paten station	120	2.110
		80	2.112
		50	2.117
		<u> </u>	2.111
		26	2.111
		15	2.111
		10	2 126
		3	2 130
	CTD 25	00	2.130
	CID 35	80	2.112
	in paten station	70 50	2.111
		<u> </u>	2.112
		40	2.111
		10	2.110
	CTD 26	150	2.114
	out of patch station	130	2.112
	out of paten station	110	2.110
		20	2.112
		<u>50</u>	2.117
		<u> </u>	2.111
		26	2.111
		15	2.114
		10	2.120
		3	2.120
08/05/04	CTD 37	150	2 112
50/ 00/ UT	In patch station	120	2 110
		100	2.110
		80	2 111
		60	4 997
		40	2 114
		26	4,225
		~~	

		15	2.128
		10	2.126
		3	4.256
	CTD 38	160	2.112
		125	2.112
		100	2.110
		60	4.227
		50	2.111
		40	2.111
		26	4.225
		15	2.128
		10	2.126
		3	4.256
09/05/04	CTD 40	170	2.112
	In patch station	120	2.110
		10	2.112
		60	4.228
		50	2.112
		40	2.112
		26	4.225
		10	2.128
		10	2.110
	CTD 41	3	4.256
	CID 41 Out patch station	40	
	optics	20	
	CTD 42	150	9 119
	out of patch station	130	2.112
	out of paten station	100	2.110
		80	2 117
		60	4 228
		50	2 111
		40	2.128
		26	4.240
		10	2.126
		3	4.258
10/05/04	CTD 43	150	2.126
	in patch	120	2.110
		100	2.112
		60	2.117
		50	4.228
		40	2.111
		26	4.225
		15	2.128
		10	2.112
		3	4.238
	CTD 45	150	2.112
	Out of patch station	130	2.110
		120	2.112
		100	2.117
		80	2.111
		60	4.222
		40	2.128
		20	4.242
		10	2.126
		3	4.256

11/05/04	CTD 46	100	2.112
Transect through	07:14 AM	60	4.224
phosphate patch		50	2.112
		26	4.245
		10	2.111
		3	4.237
	CTD 47	100	2.114
	08:30 AM	60	4.222
		50	2.128
		26	4.229
		10	2 126
		3	4 222
	CTD 48	100	2 114
	10:56 AM	60	<u> </u>
	10.007101	50	9 198
		30	2.120
		40	4,990
		20	4.229
		10	2.130
		3	4.222
	CTD 49	100	2.114
		60	4.222
		50	2.128
		40	2.126
		26	4.229
		10	2.130
		3	4.222
	CTD 50	100	2.114
	15:19 PM	60	4.222
		50	2.128
		40	2.126
		26	4.229
		10	2.130
		3	4.222
	CTD 51	100	2.114
	19:27 PM	60	4.258
		50	2.112
		40	9 196
		40	2.120
		26	4.229
		10	2.130
		2	1 999
		J	1.666
	CTD 52	100	2.114
	21:30 PM	60	4.222
	End of transect	50	2.128
		40	2.126
		26	4.229
		10	2.126
		3	4.222
12/05/04	CTD 54	160	2.112
	In patch station	140	2.112
	-	100	2.110
		80	2.117
		60	4.222
		50	2.111
		40	2 128
		10	w.1w0

		26	4.242
		10	2.126
		3	4.256
	CTD 55	120	2.130
	Optics	80	2.128
		60	
		40	
		26	
		10	
		3	
13/05/04	CTD 57	150	2.112
	Out of patch station	135	2.110
		100	2.112
		80	2.112
		60	4.228
		40	2.110
		26	4.225
		10	2.128
		3	4.256
14/05/04	CTD 59	150	2.112
	In patch station	120	2.110
	-	100	2.112
		80	2.117
		70	2.111
		60	4.225
		40	2.114
		26	4.258
		10	2.126
		3	4.222
	CTD 61	140	2.128
	out of patch station	130	2.126
		120	2.112
		100	2.111
		75	2.112
		60	4.222
		40	2.114
		26	4.227
		10	2.126
		3	4.242
15/05/04	CTD 62	150	2.112
	In patch station	130	2.110
	_	100	2.112
		80	2.117
		60	4.431
		40	2.111
		26	4.225
		10	2.128
		3	4.256
16/05/04	CTD 69	150	2.112
	T0 iron experiment	130	2.110
		120	2.112
		100	2.117
		80	2.110
		60	2.111
		40	2.112
		26	4.226
		-	

		10	2.117
		3	4.245
17/05/04	CID 71	160	4.222
	11 iron experiment	140	2.112
		130	2.112
		80	2.110
		80 60	<u> </u>
		40	2.114
		26	4.242
		10	2.126
		3	4.256
	CTD 72	160	2.112
		140	2.110
		115	2.112
		100	2.117
		80	2.111
		60	4.222
		40	2.114
		26	4.242
		10	2.126
		3	4.256
19/05/04	CTD 74	180	2.112
	In patch station	140	2.110
		120	2.112
		100	2.117
		80	<u> </u>
		40	9 114
		10	4.040
		26	4.242
		10	2.120
		3	4.236
	CID 76 Out of notch station	160	2.112
	Out of patch station	140	2.110
		110	2.112
		80	2.117
		60	4.222
		40	2.114
		26	4.242
		10	2.126
		3	4.256
20/05/04	CTD 78	3	4.229
Diel study	5:00 AM	26	4.222
	CTD 79	3	4.229
	7:00 AM	26	4.222
		160	2.112
	9.00 AIVI	140	2.11U 9.119
		100	2.112
		80	2.111
		~~	~

		60	4.225
		40	2.112
		26	4.239
		10	2.110
		3	4.256
	CTD 81	26	4.229
	10:41 AM	3	4.222
	CTD 82	150	2.112
	14:37 PM	120	2.110
		100	2.112
		80	2.117
		60	4.223
		40	2.111
		26	4 242
		3	4 256
	CTD 83	150	2 112
	16:35 PM	120	2 110
	10.001101	100	2 112
		80	2 117
		60	1 999
		40	2 112
		26	2 114
		10	2.114
		2	2.110
		26	4 220
	18·30 PM	20	4.225
	CTD 95	150	9 119
	20.35 PM	120	2.112
	20.00 1 101	100	2.110
		80	2.112
		60	2.117
		40	2.111
		40 26	2.111
		10	2.114
		2	2.120
	CTD 86	ა ეი	2.120
	C1D 00 22:30 DM	20	2.112
21 /05 /04	CTD 97	2	2.110
21/03/04		3	9 110
	00.30 AM	20	2.110
	04:40 AM	3	2 114
	04.40 AW	20	2.114
	CID 69	140	2.112
	in patch station	140	2.110
		120	2.112
		100	2.117
		80	2.128
		60	4.226
		40	2.111
		26	4.254
		10	2.111
		3	4.241
		60	4.222
	In station	26	4.229
		3	4.222
	CTD 91	160	2.112
	Out of patch station	130	2.110

		110	2.112
		100	2.117
		80	2.112
		60	4.222
		40	2.110
		26	4.242
		10	2.112
		3	4.256
22/05/04	CTD 92	150	2.112
	In patch station	120	2.110
		100	2.112
		80	2.117
		60	4.225
		40	2.111
		26	4.239
		15	2.114
		10	1.692
		3	4.256
	CTD 93	140	2.117
	Out of patch station	120	2.111
		100	2.114
		80	2.128
		60	4.222
		40	2.117
		26	4.240
		10	2.111
		3	4.258

#### Table 2 – Non toxic samples

Date	Number	Time	Volume	Position
29/04/04	1	14:22	2.111	26°35N 22°52.14W
	2	20:35	2.111	26°02N 23°30W
30/04/04	3	10:43	2.117	24°48.80N
				24°49.09W
	4	19:19	2.111	25°42.015N
				24°5468W
01/05/04	5	17:15	2.111	28°23.57N
				24°23.19W
	6	18:15	2.111	28°25.68N
				24°22.40W
02/05/04	7	16:22	2.111	27°50.56N
				23°29.75W
	8	21:55	2.110	27°55.30N
				23°18.98W
03/05/04	9	14:22	2.111	27°50.56N
				23°29.75W
	10	21:55	2.111	27°55.30N
				23°18.98W
05/05/04	10B	22:00	2.117	27°26.57N
				23°17.67W
07/05/04	11	02:44	2.111	27°42.63N
				23°17.96W
	12	18:42	2.111	27°45.61N
				23°15.89W

08/05/04	14	18:49	2.111	27°38.94N
				23°16.35W
	15	21:18	2.111	27°43.12N
				23°09.79W
09/05/04	16	19:22	2.111	27°33.16N
				23°14.56W
10/05/04	18	15:43	2.111	27°33.25N
				23°21.00W
	19	18:23	2.112	27°37.52N
				23°21.32W
11/05/04	20	16:35	2.130	27°39.18N
				23°22.25W
	21	18:40	2.130	27°39.29N
				23°22.24W
12/05/04	22	09:45	2.110	27°39.34N
				23°21.76W
13/05/04	22 B	19:28	2.112	27°53.69N
				23°28.95W
	23	20:00	2.128	27°49.90N
				23°28.95N
14/05/04	24	9:45	2.112	27°38.88N
				23°15.57W
	25	19:11	2.114	27°42.75N
				23°26.21W
16/05/04	26	9:54	2.112	27°32.41
17 /05 /04	07	10.10	0.110	22°34.32W
17/05/04	27	10:13	2.112	27°34.08N
	90	19.90	9 1 1 0	22°28.90W
	20	15.59	2.110	27°3104N
19/05/04	20	10.10	9 1 2 0	22°27.38W
16/ 03/ 04	29	10.10	2.130	27-33.2IN
	30	20.11	9 114	22°23.0W
	50	20.41	2.114	27 JO.30IN 99999 9911
19/05/04	21	18.28	2 1 1 2	22 22.32 W
10/00/04	51	10.20	<i>6.116</i>	27 40.001N 22°22 86W
	32	22:05	2 110	27°40 29N
	02	22.00	w.110	27 40.231V 22°20 02W
20/05/04	33	20.08	2 112	27°40 76N
20, 00, 01	00	~0.00	w	22°12 63W
	34	22:54		27°41 11N
				22°12 24W
21/05/04	35	19:03	2.112	27°40.05N
				22°16 40W
	36	22:29	2.110	27°41.13N
				21°58.58W
	1			

# DMS AND DMSP IN THE WATER COLUMN Stephen Archer

## Introduction and objective:

Marine emissions of DMS amount to more than half the natural flux of sulphur to the atmosphere (Andreae & Crutzen 1997). Once in the atmosphere, DMS is oxidised to sulphuric acid and methanesulphonate, forming sub-micrometer particles that scatter solar radiation and may act as cloud condensation nuclei affecting cloud radiative transfer and hence, climate (Charlson et al. 1987, Ayers & Gras 1991). One of the keys to understanding the links between biogenic DMS production and climate is to discern the processes that control DMS concentrations in seawater (Liss et al. 1997). This is known to involve a multitude of interactive biological, chemical and physical processes. Previous *in situ*, iron addition experiments in HNLC waters have generally observed an elevated production of DMSP and DMS (e.g. IRONEX, SOIREE) that may help explain the link between ice-core records of DMS production and global temperature (Turner et al. 1991). Although more recent experiments (e.g. SERIES, SAGE) suggest the link may be more complex than first thought. The objective of this work was to examine the impact of alleviating nutrient limitation (potentially phosphate and/or iron) on reduced sulphur cycling in the oligotrophic sub-tropical Atlantic.

#### **Methods:**

### DMS and DMSP concentrations:

Seawater samples collected at discrete depths were filtered through GF/F filters using a syringe pump at a standard flow rate of 5 ml min⁻¹. In the process, the filtrate was injected directly into a purge chamber and purged with nitrogen, the volatiles being trapped over liquid nitrogen for quantification of DMS. Filters were transferred to sealed vials or frozen in liquid nitrogen. The majority odf DMSPp samples will be analysed at PML. DMSPp is hydrolysed to DMS in 0.5 M NaOH. Similarly, the purged filtrate was retained for hydrolysis of dissolved DMSP to DMS. DMS was quantified on a Varian 3800 gas chromatograph with PFPD detector.

#### DMSPp production and consumption rates:

A dilution approach (see Kimmance, this report), was used to quantify the specific production rate of DMSP by phytoplankton and the rate that DMSP was consumed by grazers. The dilution series generated a gradient of grazing pressure. Subsamples were filtered for DMSPp quantification at the beginning and end (T24) of incubations allowing an instantaneous production rate to be calculated for varying levels of dilution/grazing pressure.

#### DMSP vs. SF₆ and nutrient availability:

On two occasions, once per patch, the non-toxic supply was used to obtain discrete, nearsurface water samples collected at 5 min intervals during transects of the fertilised patch.

#### Diel examination of DMS(P) concentrations:

One diel study of DMS and DMSP concentrations was made, involving sampling at 3m and 26 m at 2 hourly intervals for > 24 hours. SF6 concentrations were monitored continuously in order to ensure sampling was undertaken from the same water mass during the study.

Date	CTD in	Depths	CTD out	Depths	DMSPp measured in dilution expts.	Mapping transects
30-Apr			010	3,120		
01-May			012	3,10,50,110,200,300,		
02-May			015	3,10,50,125,200,300,		
03-May			028	3,10,40,60,100,135,160,200		
04-May			029	3,10,40,65,115,120,140,200		

#### The table below details the nature, timing and depth of samples used and the timiing of experiments.

05-May	030	3,10,26,40,50,60				
06-May	031	3,10,26,40,60,120,200				
07-May	034	3,10,26,40,50,60				
	035	3,10,26,40	036	3,10,26,40,50,60		
08-May	037	3,10,26,40,50,60,120	038	3,10,26,40,60		
09-May	040	3,10,26,40,50,60	041	3,10,26,40	#6	
			042	3,10,60		
10-May	043	3,10,26,40				
	044	3,10,26,40	045	3,10,26,40		
11-May	T1-T7	3,10,40				
12-May	054	3,10,26,40,60,75,120			#7	
	055	3,10,40				
13-May	056	DMSPp: 3,16,60				
	057	3,10,26,40,60,75				
14-May	059	3,10,26,40,60,120			#8	
	060	3,10,26,40	061	3,10,26,40		
15-May	062	3,10,26,40				#1
16-May	069	3,10,26,40,60,130				
17-May	071	3,10,40,60,120	072	3	#9	
18-May						
19-May	074	3,10,26,40,60,80,110			#10	
	075	3,10,26	076	3,10,26,40,110,200		
20-May	diel 1-11	3,26				
21-May	089	3,26,40,200			#11	
	090	3,26,60,120	091	3,10,26,40,60		
22-May	092	3,10,26,40,60,120	093	2,10,26,60,120,200		#2,#3

# **Preliminary results:**

<u>DMS</u>, dissolved DMSP (DMSPd) and particulate DMSP (DMSPp) concentrations: DMS and DMSPd concentrations in the region of the experiments were higher than I expected, ranging from 1.5 to 2.5 nM for DMS and > 3 nM for DMSPd in the mixed layer. On the other hand, DMSPp concentrations appeared to be relatively low, ranging from 11 to 16 nM. Figure 1 illustrates a typical depth profile for DMS, DMSPd and DMSPp.

Figure 1.



Initial indications are that DMS concentration in both fertilised patches remained similar to surrounding waters. During the first addition, DMS concentrations dropped steadily

throughout the study, but with no obvious deviation from surrounding waters Figure 2. Whilst in the second addition, they remained more constant. Trends in DMSPd and DMSPp way show a different story. Interestingly the diel study may have exposed a diel cycle in DMS concentration in these oligotrophic, high irradiance waters. In consequence the time of sampling is an important consideration in interpreting the results of the DMS study and our strategy of a routine sampling programme (in patch morning, out of patch afternoon) may have been flawed in hindsight. There are relatively few measurements of DMS in such waters and even fewer with the additional 'supporting' data available that is afforded by this experiement, particularly the Lagrangian aspect. It also illustrates the fairly steady-state nature of reduced sulphur cycling in these waters. Hopefully, DMSPp production rates derived from the dilution experiments may throw more light on the impact of nutrient addition on DMS(P) cycling.



Figure 2. Addition #1

#### **Acknowledgements:**

I would like to thank: Nick Owens, Phil Nightingale and Andy Rees for setting-up the experiment; the Captain and Crew of RRS Charles Darwin for the high quality of the service onboard. Financial support was from: Plymouth Marine Laboratory; the NERC; and the Royal Society of New Zealand.

#### IODOCARBON CONCENTRATIONS IN THE WATER COLUMN DURING FEEP Laura Goldson Introduction and Objectives

The oceans are the primary source of iodine to the atmosphere. While volatile iodinated compounds are known to play a role in tropospheric ozone chemistry, their marine production/destruction mechanisms are poorly understood. During CD156 concentrations of iodomethane, iodoethane, chloroiodoethane and diiodomethane were measured in seawater to determine the response of these compounds to iron/phosphate fertilisation. In addition, a diel study was carried out with mixed layer samples taken approximately every two hours for a twenty four hour period to examine photochemical iodocarbon production/destruction.

# Methods

Seawater was collected into 300 ml glass stoppered amber bottles from the CTD 10 L Niskin bottles. Iodocarbon analysis was then carried out on 40 ml sub-samples injected manually into the purge tower through a GFF filter. Iodocarbons were purged from the seawater with BIP Nitrogen for 20 minutes and trapping over liquid  $N_2$  at a temperature of -150°C. Iodocarbon concentrations were measured by gas chromatography with electron capture detection (GC-ECD). Instrument calibration was performed periodically by injection and measurement of known volumes of iodomethane from a calibrated permeation device (KINTEK) maintained at 30°C in a water bath (GRANT).

A combination of vertical profiles (3 – 200 m) (Figure 1) and mixed layer samples were analysed to determine both the iodocarbon response to fertilisation and possible temporal daily cycling (Figure 2), respectively. All of the CTD stations sampled are listed in Table 1.

Detailed vertical profiles were sampled and analysed prior to the release of phosphate and/or iron. These pre-release analyses, taken to determine background iodocarbon concentrations, will permit assessment of iodocarbon response to fertilisation. Companion data (e.g. phytoplankton and bacterial numbers, temperature, salinity and chlorophyll concentrations) will not only allow distinctions between water masses to be made, thereby identifying natural variability, but may help elucidate causal processes contributing to the production/destruction of these iodocarbons.



*Figure 7: Concentration of iodomethane (pg ml-1) versus pressure (db) from typical CTD cast (CTD_40 T_10 Patch 1 IN).* 



Figure 8: Iodomethane concentration (pg ml⁻¹) at 26 m water depth from dawn til dusk.

#### **Preliminary Results.**

Iodomethane, iodoethane and chloroiodoethane were found at easily detectable concentrations both before and after the fertilisations. Diiodomethane was often undetectable within the euphotic zone on daily vertical casts but generally measurable at depths in excess of 100 metres. While preliminary analysis of the data revealed no marked response to phosphate or phosphate/iron fertilisation, further detailed analyses of iodocarbon concentrations in conjunction with the companion data are required. Vertical distribution patterns of certain compounds were apparent in both fertilised and natural waters (i.e concentration maxima for chloroiodoethane were strongly correlated with the chlorophyll a maxima). Further examination of the companion data may reveal possible mechanisms responsible for the variations in iodocarbon vertical distributions. Preliminary results of the diel study show a temporal cycling of iodomethane at 26 metres water depth with an increase in concentration from dawn to dusk (Figure 2), implying possible photochemical production. Additional processing of the remaining iodocarbon data is necessary in order to ascertain whether similar temporal cycling occurred for the other compounds.

DATE	TIME	CTD	STN	IN/OUT	SURF ONLY
28/4/2004	14:10	4	PR	PR	Ν
29/4/2004	10:15	7	PR	PR (IM4)	Ν
29/4/2004	18:38	8	PR	PR (IM5)	Ν
30/4/2004	8:40	10	PR	PR (IM7)	Ν
1/5/2004	9:59	12	PR	PR (IM9)	Ν
2/5/2004	8:25	15	PR	PR (IM12)	Ν
3/5/2004	10:18	28	PR	PR (IM25)	Ν
4/5/2004	8:43	29	T_zero	PR	Ν
5/5/2004	19:13	30	T_1	IN	Ν
6/5/2004	04:08	31	T_2	IN	Ν
6/5/2004	7:15	32	T_3	IN	Ν
7/5/2004	15:51	36	T_7	OUT	Ν
8/5/2004	11:12	37	T_8	IN	Ν
8/5/2004	15:48	38	T_9	OUT	Ν
9/5/2004	7:34	40	T_10	IN	N
9/5/2004	15:20	42	T_13	OUT	N

Table 1: CTD stations sampled for iodocarbon analysis during CD156

10/5/2004	7:36	43	T_14	IN	Ν
10/5/2004	14:59	45	T_16	OUT	Y
11/5/2004	6:09	46	T_17 trans1		Y
11/5/2004	8:07	47	T_18 trans1	OUT	Y
11/5/2004	10:07	48	T_19 trans1		Y
11/5/2004	12:12	49	T_20 trans1		Y
11/5/2004	14:13	50	T_21 trans1		Y
11/5/2004	18:36	51	T_22 trans1		Y
11/5/2004	20:32	52	T_23 trans1	OUT	Y
12/5/2004	7:04	54	T_25	IN	Ν
12/5/2004	14:09	55	T_26	OUT	Ν
13/05/04	16:12	57	T_28	IN	Ν
14/05/04	7:19	59	T_30	IN	Ν
14/05/04	12:05	60	T_31	IN	Ν
14/05/04	14:48	61	T_32	OUT	Ν
15/05/04	7:16	62	T_33	IN	Ν
16/05/04	4:34	69	TB_zero	OUT	Ν
17/05/04	7:04	71	TB_2	IN	Ν
17/05/04	13:57	72	TB_3	IN	Y
19/05/04	7:21	74	TB_5	IN	Ν
19/05/04	8:30	75	TB_6	IN	Ν
19/05/04	14:55	76	TB_7	OUT	Ν
20/05/04	4:28	78	diel_1	IN	Ν
20/5/04	6:49	79	diel_2	IN	Ν
20/05/04	8:12	80	diel_3	OUT	Ν
20/05/04	10:19	81	diel_4	IN	Ν
20/05/04	14:00	82	diel_5	IN	Ν
20/05/04	16:08	83	diel_6	IN	Ν
20/05/04	18:05	84	diel_7	IN	Ν
20/05/04	20:06	85	diel_8	IN	Ν
20/05/04	22:07	86	diel_9	IN	Ν
21/05/04	0:06	87	diel_10	IN	N
21/05/04	4:11	88	diel_11	IN	Ν
21/05/04	7:06	89	TB_9	IN	Ν
21/05/04	16:00	91	TB_11	OUT	Ν
22/5/04	8:16	92	TB_12	IN	Ν

# METHYL BROMIDE MEASUREMENTS DURING FEEP Malcom Liddicoat & Phil Nightingale

### Introduction

Methyl bromide is a volatile, toxic compund with a high ozone deopleting potential. It is botyh produced in seawater by some species of marine phytoplankton and thought to be consumed by marine bacteria. Much of the world's oceans are thought to be close to equilibrium with respect to the atmosphere. Our aims for this cruise were to

- 1. Determine the levels of methyl bromide in part of the oligotrphic oceans an area with few existing data.
- 2. Determine whether the oceans were acting as a source or a sink of methyl bromide
- 3. Test whether the addition of iron and/or phosphate had any impact on dissolvesd methul bromide levels.

#### Methods

Methyl bromide dsamples were collected from the CTd rosette using 500 ml ground glass bottles. CH₃Br was sparged from seawater using nitrogen gas and then cryogenically focused on a 1/16" stainless steel trap at –150 °C. The sample was , thermally desorbed at 100 °C and the mixture separated by a DB-624 capillary column (0.53 mm ID x 75 m), and then detected by electron captureN₂ [*Krysell and Nightingale*, 1994]. The analytical uncertainties were estimated as 2 % for the sample from the headspace and 5 % for the dissolved gas.

### Samples

The following samples were collected and analysed for methyl bromide,

Date & Time	CTD cast	Depths Sampled
28/04/2004 14:10	4	300, 50, 25, 10, 3
29/04/2004 10:15	7	300, 120, 10
29/04/2004 18:40	8	25, 10
30/04/2004 08:40	10	300, 50, 25, 10, 3
01/05/2004 09:59	12	300, 110, 25, 10, 5
02/05/2004 08:25	15	10
05/05/2004 19:13	30	200, 10, 3
06/05/2004 07:15	32	80, 50, 15, 3
07/05/2004 07:45	34	26, 10
07/05/2004 13:29	35	26, 15
08/05/2004 11:12	37	80, 26, 10
08/05/2004 15:50	38	26, 10
09/05/2004 07:34	40	26, 10
09/05/2004 12:40	41	26, 10
09/05/2004 15:20	42	26, 10
10/05/2004 07:36	43	26, 15, 10
10/05/2004 12:30	44	26
10/05/2004 14:59	45	26, 10
11/05/2004 06:09	46	26, 10
11/05/2004 08:07	47	26, 10
11/05/2004 10:07	48	26, 10
11/05/2004 12:12	49	26, 10
11/05/2004 14:13	50	26, 10
11/05/2004 18:36	51	26, 10
12/05/2004 07:05	54	26, 10
12/05/2004 14:09	55	26, 10
13/05/2004 16:12	57	26
14/05/2004 07:19	58	26, 10, 3
14/05/2004 14:48	59	10, 3

10/00/2004 01:10 00	, ,
19/05/2004 07:21 65	26, 3
19/05/2004 12:07 66	10, 3
19/05/2004 15:50 67	10, 3
20/05/2004 08:12 80	10, 3
21/05/2004 07:06 89	10, 3
22/05/2004 08:16 92	10, 3
22/05/2004 11:38 93	10, 3

# Results

Methyl bromide data from the tropical North Atlantic Ocean ranged from about 1.2 pmol dm⁻³ (60% saturated) up to 3.1 pmol dm⁻³ (160% saturated). The mean saturation level of methyl bromide in seawater with respect to the atmosphere was about 120%, indicating that the oceans in this area were a net source of methyl bromide to the atmosphere. We have yet to find any evidence that addition of iron and/or phosophate impacted on the cycling of methyl bromide, although data analysis is at an early stage.

# QUANTIFYING PHYTOPLANKTON GROWTH RATES, GRAZING MORTALITY, AND VIRAL LYSIS, USING THE DILUTION TECHNIQUE. *Susan Kimmance*

# Introduction

Lysis by viruses and grazing by protozoa represent two fundamentally different pathways by which carbon and nutrients may cycle within a food web. Viral lysis diverts primary production away from higher trophic levels as a result of completely transforming phytoplankton cells to DOM, cell fragments, and inorganic nutrients. This contrasts with the fate of primary production when cells are grazed. It has been estimated that  $\geq 26\%$  of primary production may be channelled through the 'viral shunt' to DOM as a result of viral lysis of phytoplankton, bacterioplankton and grazers. However, no techniques currently exist to directly quantify the viral component of phytoplankton mortality. This work was a component of a NERC-funded grant aimed at developing a highly promising dilution technique to directly quantify viral mortality of specific phytoplankton in natural waters.

The autotrophic prokaryotes are considered to be major primary producers in nutrientlimited gyres of subtropical and tropical oceanic provinces. The cyanophages (viruses) that infect them are known to influence nutrient cycling, mediate species succession and act as vectors for horizontal gene transfer. The ecology of viruses in oligotrophic regions is poorly understood, but previous nutrient addition experiments have suggested that nutrient limitation, specifically phosphorus limitation, may inhibit viral production. Additionally, many virus receptors are linked to high affinity iron uptake channels in host cells. This may have an interesting ecological effect in iron-limited conditions; thus, if cells produce such channels to scavenge Fe, they may also inadvertently attract a virus, though this hypothesis has never been tested. The FeEPO4 cruise provided the opportunity to test laboratory developed methods in natural waters and investigate the effect of nutrient addition (phosphate and iron) on viral productivity.

# Methods:

# **Dilution experiments:**

A series of on-deck incubation experiments were conducted to:

- quantify the mortality of phytoplankton cells through viral lysis compared to that of grazing (flow cytometry, chl a analysis, microscopy).
- assess the physiological effects of the dilution experiment methodology on phytoplankton species using: fast repetition rate fluorometry (FRRF), flow cytometry (AFC), and cell-cycle analysis.
- quantify the production rates of phytoplankton DMSP, the taxa responsible for that production and the loss of phytoplankton DMSP through grazing and viral lysis (see Archer, this report).

To set up dilution incubations, fresh seawater was siphoned into clean 20 L polypropylene carboys from a CTD system containing 24 x 10 L Trace Metal Niskin bottles, from CTD casts at 26 m depth. Two series of dilution incubations were set-up in parallel, one using diluent filtered through a 0.2  $\mu$ m pore size filter and the second through a 30 kDa tangential flow system. The diluent and whole water were added to 10 L polypropylene carboys in the correct proportions to create the t0 dilutions, i.e., 20, 40, 70 and 100% whole water. These dilutions created a gradient of grazing pressure. Triplicate 1L polycarbonate bottles were filled from each t₀ carboy and placed into the on-deck incubators with neutral density screening providing 33 % light. Sub-samples were taken from the t0 carboys for phytoplankton abundance (live, AFC), chl a analysis, phyto-physiology (FRRF), DMSP (see Archer, this report), virus abundance (fixed, AFC), virus productivity (live plaque assays), and grazer abundance (Lugol's fixed, microscopy). Samples for fixed viral analysis were preserved with glutaraldehyde (0.5% final concentration) for 30 mins at 4°C, flash frozen in liquid nitrogen for 50 s and stored at -80°C. Sampling was repeated at t24 from the triplicate

1L polycarbonate bottles. Viral lysis rates, grazing rates, and phytoplankton growth rates, were determined from changes in chl a and phytoplankton abundance in the 1L experimental bottles between t0 and t24.

# Viral productivity:

In addition to the virus measurements taken during the dilution incubations, a series of experiments were conducted to measure temporal changes in viral productivity before and after the nutrient additions. The rate of viral production was determined from the production rate of new viral particles after the dilution of the in situ viral community. Water from 26 m was collected from CTD casts and gently vacuum filtered through 47 mm diameter, 0.2  $\mu$ m pore-size Supor membrane filters (Pall Gellman). During this process, the sample was kept mixed, while volume was maintained (>50 ml, final volume = 300 ml) by adding virus-free, ultrafiltered seawater (30 kDa). This resulted in viruses being diluted to ~10-20 % of the initial abundance. Samples (50 ml) of this virus-reduced retentate were placed in 250 ml polycarbonate bottles and incubated in the dark. Sub-samples (2 ml) for viral enumeration, were collected every 3 h and fixed with glutaraldehyde (0.5 % f.c.) for 30 mins at 4°C, flash frozen in liquid nitrogen for 50 s and stored at -80°C, for analysis back at PML. Virus production rates will be determined from regressions of viral abundance vs. time for triplicate incubations

# <u>Diel study:</u>

One diel study of phytoplankton abundance, photo-physiology (FRRF), cell cycle analysis and viral abundance was undertaken. This involved sampling from within the second patch (Fe + PO₄), from CTD casts at 3 and 26 m, at ~2 hourly intervals for 24 hours. Samples for cell-cycle analysis, phytoplankton, and viral abundance were fixed with glutaraldehyde (0.5% final) for 30 mins at 4°C, flash frozen in liquid nitrogen for 50 s and stored at –80°C, for analysis back at PML.

# Routine sampling:

In addition, routine sampling inside the Lagrangian patch and in adjacent waters was conducted to provide vertical profiles and information on temporal shifts in the viral composition, abundance and productivity, and host diversity (DNA >0.45 $\mu$ m fraction and virus <0.2 $\mu$ m fraction) in response to the nutrient additions.

# Preliminary results:

Preliminary data from the dilution experiments show varying trends in response to the nutrient additions. Dilution FRRF results suggest an increase in  $t_0$  phytoplankton Fv/Fm within fertilised patches compared to initial unfertilised waters. This infers that the nutrient additions improved phytoplankton photo-physiology and was consistent for both additions. From the data analysed so far, it appears that there was a significant increase in microzooplankton grazing rates and phytoplankton growth rates as a result of the addition during patch 1 (+ PO₄). There was no significant response during patch 2 (+ Fe and PO₄). Parameters from dilution experiments and routine sampling still to be analysed are: nutrient data, chlorophyll, DMSPp production, host diversity and virus samples. Once these data have been obtained and comparisons made with SF₆ data, results may become clearer.

Table 1 summarises the CTD casts sampled and analyzed during the cruise (FV = glut fixed virus samples; LV = live virus samples; VP = viral productivity experiment; FP = fixed phytoplankton samples, and LFG = Lugol's fixed samples for microzooplankton analysis, (for AFC, FRRF and DMSP, see above).

DATE	CTD#	TIME (GMT	DEPTHS SAMPLED	BOTTLE NOS.	PARAMETERS MEASURED
28-Apr	CD156_002	) 06:30	60m	13, 14, 15	Dilution1 (Chl a, nutrients, AFC, FRRF, FV)
29-Apr	CD156_007	09:30	60m	17, 18, 19, 20	Dilution2 (Chl a, nutrients, AFC, FRRF, FV)
30-Apr	CD156_010	09:40	60m	20	Synechococcus cell cycle
1-May	CD156_011	04:30	60m	7, 8, 9, 13, 14	Dilution 3 (Chl a, nutrients, AFC, FRRF, FV)
2-May	CD156_015	09:23	25m	15,16,17,18,19,20,21 .22,24	Dilution4 (Chl a, nutrients, AFC, FRRF, FV)
3-May	CD156_028	10:30	3,10,25,40,50,60,75	, ,	Synechococcus/ Prochlorococcus survival expt
4-May	CD156_029	08:43	3-300m		FV, LV and VP (26m)
6-May	CD156_031	04:30	26m	7-16	Dilution5 (Chl a, nutrients, AFC, FRRF, FV, LV)
7-May	CD156 034	08:45	3,10,15,26,40,50	18-23	FV
7-May	CD156_035	14:17	3,10,15,26,40,50,60	17-23	FV and VP (26m)
8-May	CD156_037	12:24	26m	20	FV, LV and host diversity (DNA)
9-May	CD156_039	04:30	26m	7-19	Dilution6 - Chl a, nutrients, AFC,FRRF,FV,LV,DMSP,LFG
10-May	CD156_044		26m	20	VP
11-May	CD156_046	07:00	3,10,26,40,50,60	17,18,19,20,22,24	FV,LV,VP,host diversity, DNA
11-May	CD156 047	08:50	3,10,26,40,50,60	17,18,19,20,22,24	FV
11-Mav	CD156_048	10:56	3,10,26,40,50,60,70	14.17.18.19.20.22.24	FV.LV.VP.host diversity, DNA
11-May	CD156_050	14:59	3.10.26.40.50.60.70	14.17.18.19.20.22.24	FV. LV
11-May	CD156_051	19.21	3 10 26 40 50 60 70	14 17 18 19 20 22 24	FV LV
12-May	CD156_053	04.30	26	11,17,10,17,20,22,21	Dilution7 (Chla nutrients
12-1 <b>v</b> 1ay	CD150_055	04.50	20		AFC FRRF FV LV DMSP LFG
14-May	CD156_058	04:30	26m		Dilution8 (Chla, nutrients, AFC,FRRF,FV,LV,DMSP,LFG
15-May	CD156_062	08:26	26m	21	VP and host diversity (DNA)
16-May	CD156 069	05:38	3,10,26,40,60,70,80	16,17,18,19,20,22,24	FV, LN
17-May	CD156_070	04:30	26m	7-18	Dilution9 (Chl a, nutrients,
17-May	CD156_072	15:00	3,10,26,40,60,80,90,120	11,15,16,18,19,20,22, 24	FV, LV (26, 120m)
19-May	CD156_073	04:30	26m		Dilution10 (Chl a, nutrients, AFC,FRRF,FV,LV,DMSP,LFG
20-May	CD156_078	05:30	3 and 26m		FP, FV, FRRF, cell cycle
20-May	CD156_079	06:49	3 and 26m		FP, FV, FRRF, cell cycle
20-May	CD156 080	08:12	3 and 26m		FP, FV, FRRF, cell cycle
20-May	CD156_081	10:19	3 and 26m		FP. FV. FRRF. cell cycle
20-May	CD156_082	14.00	3 and 26m		FP FV FRRE cell cycle
20 May	CD156_083	16.08	3 and 26m		FP FV FRRF cell cycle
20 May	CD156_084	18.05	3 and 26m		FP FV FRRE cell cycle
20-May	CD156_085	20.06	3 and 26m		FD EV EDDE cell cycle
20-iviay	$CD150_003$	20.00	3 and 26m		ED EV EDDE gall avala
20-iviay	$CD150_080$	22:07	3  and  26  m		FF, FV, FKKF, CEII CYCIE
20-1vlay	$CD156_08/$	00:06	5  and  26m		FP, FV, FKKF, Cell Cycle
20-May	CD156_088	04:11	3 and 26m		FP, FV, FKKF, cell cycle
20-May	CD156_089	07:06	3 and 26m		FP, FV, FRRF, cell cycle
21 <b>-</b> May	CD156_090	04:30	26m		Dilution11 (Chl a, nutrients, AFC,FRRF,FV,LV,DMSP,LFG
22-May	CD156_092	8:16	3-200m		FV

#### **DEPLOYMENT OF UOR** *Nicholas Owens*

### Introduction

A PML built Undulating Oceanographic Recorder (UOR) was deployed in order to help identify suitable locations for Patch 1 and Patch 2 and when the vessel was used in survey/mapping mode (typically overnight). The following instruments were mounted within the UOR,

- 1. A Sea-Bird 19+ CTD (SN 4180)
- 2. A Chelsea Technologies MiniTracka fluorometer (SN 175024)
- 3. A Chelsea Technologies AquaTracka Mk II, Beam Transissometer (SN 161/2642/006)

### Deployment

Tows are summarised below,

Tow	Start					Finish				
	<u>Yr</u>	<u>Month</u>	<u>Day</u>	Hours	<u>Min</u>	<u>Yr</u>	<u>Month</u>	<u>Day</u>	<u>Hours</u>	Min
uor1	2004	4	28	1	11	2004	4	28	6	33
uor2	2004	4	28	8	4	2004	4	28	13	34
uor3	2004	4	28	20	15	2004	4	29	3	44
uor4	2004	4	29	5	15	2004	4	29	9	23
uor5	2004	4	29	13	9	2004	4	29	18	22
uor6	2004	4	29	19	37	2004	4	30	0	22
uor7	2004	4	30	1	32	2004	4	30	8	19
uor8	2004	4	30	14	37	2004	5	1	9	32
uor9	2004	5	1	12	17	2004	5	1	17	29
uor10	2004	5	1	18	57	2004	5	1	23	44
uor11	2004	5	2	0	25	2004	5	2	5	24
uor12_1	2004	5	3	15	45	2004	5	3	16	58
uor12_1a	2004	5	3	16	58	2004	5	3	17	21
uor12_2	2004	5	3	17	18	2004	5	3	18	18
uor12_2a	2004	5	3	18	18	2004	5	3	18	44
uor12_3	2004	5	3	18	44	2004	5	3	19	45
uor12_3a	2004	5	3	19	43	2004	5	3	20	10
uor12_4	2004	5	3	20	9	2004	5	3	21	31
uor13_1	2004	5	8	20	6	2004	5	8	21	7
uor13_2	2004	5	8	21	7	2004	5	8	21	49
uor13_3	2004	5	8	21	49	2004	5	8	22	39
uor13_4	2004	5	8	22	39	2004	5	8	23	34
uor13_5	2004	5	8	23	34	2004	5	9	0	29
uor13_6	2004	5	9	0	29	2004	5	9	1	2
uor14_1	2004	5	9	17	4	2004	5	9	19	32
uor14_2	2004	5	9	19	32	2004	5	9	20	39
uor14_3	2004	5	9	20	39	2004	5	9	22	5
uor14_4	2004	5	9	22	5	2004	5	9	23	57
uor14_5	2004	5	9	23	57	2004	5	10	1	39
uor14_6	2004	5	10	1	54	2004	5	10	3	47
uor14_7	2004	5	10	3	47	2004	5	10	5	10
uor17_1	2004	5	13	20	53	2004	5	13	21	23
uor17_2	2004	5	13	21	23	2004	5	13	22	46
uor17_3	2004	5	13	22	46	2004	5	13	23	48
uor17_4	2004	5	13	23	48	2004	5	14	1	2
uor17_5	2004	5	14	1	2	2004	5	14	1	55
uor17_6	2004	5	14	1	55	2004	5	14	3	2
uor17_7	2004	5	14	3	2	2004	5	14	3	49

uor18_1	2004	5	19	19	59	2004	5	19	20	23
uor18_2	2004	5	19	20	23	2004	5	19	21	7
uor18_3	2004	5	19	21	7	2004	5	19	21	47
uor18_4	2004	5	19	21	47	2004	5	19	22	27
uor18_5	2004	5	19	22	27	2004	5	19	23	8
uor18_6	2004	5	19	23	8	2004	5	20	0	20
uor18_7	2004	5	20	0	20	2004	5	20	1	26
uor18_8	2004	5	20	1	26	2004	5	20	2	34
uor18_9	2004	5	20	2	34	2004	5	20	3	33
uor19-1	2004	5	21	20	13	2004	5	21	22	52
uor19-2	2004	5	21	22	52	2004	5	21	23	27
uor19-3	2004	5	21	23	27	2004	5	22	0	42
uor19-4	2004	5	22	0	42	2004	5	22	1	57
uor19-5	2004	5	22	1	57	2004	5	22	3	0
uor19-6	2004	5	22	3	0	2004	5	22	4	11
uor19-7	2004	5	22	4	11	2004	5	22	5	36
uor19-8	2004	5	22	5	36	2004	5	22	6	31

#### UKORS REPORT Terry Edwards

### **Rosette Configuration**

- 24 way titanium frame
- OTE 10 litre sample bottles, trace metal free
- Distance from pressure sensor to bottle to be confirmed
- No RTM fitted.

The .con file on the data disc gives a rundown of all sensors, channels and cals for that specific cast.

#### **Met Sensors**

- All met and light sensors are mounted on the foremast.
- Wind vane 0/360 deg is aft.
- Height above sea level: barometer, 14.5m, wind sensors 16m
- Pumped sea water inlet 6m below sea level.

#### **Surfmet Sensor Information : Main**

Manufacturer	Sensor	Serial no	Comments
FSI	OTM temperature	1361	
FSI	OTM temperature	1370	
Wetlabs	fluorometer	134	
Seatech	transmissometer	1019D	
Vaisala	Barometer PTB100A	S3440009	
Vaisala	Temp/humidity HMP44L	S504004	
ELE	PAR DRP5	5143	port
ELE	PAR DRP5	5145	stb
Kipp and Zonen	TIR CMB6	92276	port
Kipp and Zonen TIR CMB6		962301	stb
Sensors without cal			
FSI	OCM conductvity	1358	
Vaisala	Sensor collector QLI	R381006	
Vaisala	Anemometer WAA	22306	
Vaisala	Wind vane WAV	21213	
Rhopoint	+/- 5v	9205	
Rhopoint	+/- 5v	9347	

# **STATION LOG**

CTD					
Number	Name	Date	Time	Lat	Lon
CTD_1	TEST	26-Apr-04	13:48:31	16.5323	27.9132
CTD_2	IM7	27-Apr-04	23:51:53	21.9988	27.9645
CTD_3	IM8	28-Apr-04	06:56:21	22.694	27.3627
CTD_4	IM9	28-Apr-04	13:57:44	23.4395	27.9638
CTD_5	IM10	28-Apr-04	19:31:43	23.816	27.9703
CTD_6	IM11	29-Apr-04	03:48:19	23.4667	26.7587
CTD_7	IM12	29-Apr-04	10:02:00	6.0672	26.7128
CTD_8	IM13	29-Apr-04	10:02:00	7.398	12.1358
CTD_9	IM14	30-Apr-04	00:37:55	23.9765	25.601
CTD_10	IM15	30-Apr-04	08:20:59	24.8263	24.8223
CTD_11	IM16	01-May-04	04:25:02	25.0262	27.1632
CTD 12	IM1	01-May-04	09:43:09	25.0243	27.807
CTD_13	IM17	01-May-04	17:45:55	24.3743	28.4183
CTD_14	IM18	01-May-04	23:42:21	23.6235	28.6392
CTD 15	IM19	02-May-04	08:16:42	23.513	27.9042
CTD_16	IM20	02-May-04	16:04:20	23.493	27.8415
CTD_17	IM21	02-May-04	17:14:48	23.4365	27.8922
CTD_18	IM22	02-May-04	20:55:04	23.3328	27.974
CTD 19	IM23	02-May-04	22:23:17	23.3003	27.8937
CTD 20	IM24	02-May-04	23:35:52	23.3653	27.8362
CTD 21	IM25	03-May-04	00:54:00	23.4338	27.7763
CTD 22	ТО	03-May-04	02:08:20	23.3653	27.7167
CTD 23	IM1	03-May-04	03:24:37	23.2987	27.7778
CTD 24	T1IN	03-May-04	04:38:11	23.2345	27.8343
CTD 25	T1IN2	03-May-04	05:54:03	23.1687	27.7768
CTD 26	T3IN	03-May-04	07:12:17	23.2363	27.7183
CTD 27	T4IN	03-May-04	08:16:30	23.3012	27.6583
CTD 28	T5IN	03-May-04	10:08:05	23.3327	27.8108
CTD 29	T6IN	04-May-04	08:30:08	23.3315	27.8128
CTD 30	T7OUT	05-May-04	19:07:37	23.3113	27.7872
CTD 31	T8IN	06-May-04	03:54:39	23.2805	27.7687
CTD 32	T9OUT	06-May-04	07:06:59	23.283	27.756
CTD 33	T10	06-May-04	12:27:51	23.2843	27.7472
CTD 34	IM2	07-May-04	07:39:20	23.2198	27.7232
CTD 35	T11IN	07-May-04	13:18:59	23.2212	27.7345
CTD 36	T12IN	07-May-04	15:43:29	23.3482	27.7363
CTD 37	T13OUT	08-May-04	10:45:00	23.2366	27.6876
CTD 38	T14IN	08-May-04	15:45:00	23.0483	27.6905
CTD 39	T15IN	09-May-04	04:24:00	23.2585	27.6605
CTD 40	T16OUT	09-May-04	07:23:00	23.2299	27.6913
CTD 41	T17IN	09-May-04	12:33:24	23.2268	27.7038
CTD 42	T18TRAN1	09-May-04	15:11:04	23.2295	27.7913
CTD 43	T29TRAN1	10-May-04	07:31:51	23.2207	27.6582
CTD 44	T20TRAN1	10-May-04	12:19:00	23.2207	27.6583
CTD 45	TheNoMooring	10-May-04	14:50:15	23.3452	27.5525
CTD 46	T21TRAN1	11-May-04	05:57:46	23.3543	27.664
CTD 47	T22TRAN1	11-May-04	07:46:23	23.3043	27.7125
CTD 48	T23TRAN1	11-Mav-04	09:58:42	23.328	27.692
CTD 49	t24	11-May-04	11:59:01	23,3393	27,6765
CTD 50	T25IN	11-May-04	13:56:07	23.356	27.6642
CTD_51	T26IN	11-May-04	18:33:11	23.3703	27.6543

CTD_52	T27IN	11-May-04	20:28:04	23.4093	27.6183
CTD_53	T28IN	12-May-04	03:57:30	23.3697	27.661
CTD_54	t29in	12-May-04	06:53:50	23.3685	27.6635
CTD_55	t30in	12-May-04	13:33:53	23.3597	27.6677
CTD_56	IM3	13-May-04	12:08:15	23.4217	27.7103
CTD_57	t31in	13-May-04	14:33:16	23.4373	27.7025
CTD_58	t32OUT	14-May-04	04:30:28	23.2703	27.6153
CTD_59	t32in	14-May-04	07:10:50	23.2713	27.6165
CTD_60	S001	14-May-04	11:55:53	23.274	27.6295
CTD_61	S002	14-May-04	14:43:05	23.1925	27.6862
CTD_62	S003	15-May-04	07:05:51	23.238	27.6153
CTD_63	S004	15-May-04	14:37:30	22.6628	27.62
CTD_64	S005	15-May-04	15:57:45	22.5707	27.538
CTD_65	S006	15-May-04	17:15:49	22.4802	27.4558
CTD_66	TB00	15-May-04	19:04:41	22.4777	27.6203
CTD_67	IM4	15-May-04	20:17:12	22.5682	27.6205
CTD_68	TB01	15-May-04	22:06:23	22.5725	27.4572
CTD_69	TB02	16-May-04	04:24:42	22.5715	27.539
CTD_70	TB03	17-May-04	04:04:19	22.4992	27.5462
CTD_71	TB04	17-May-04	06:54:49	22.4922	27.5547
CTD_72	TB05	17-May-04	13:24:01	22.4618	27.5658
CTD_73	TB06IN	19-May-04	03:56:07	22.321	27.6647
CTD_74	TB07OUT	19-May-04	06:56:13	22.3148	27.6588
CTD_75	TB08OUT	19-May-04	11:34:54	22.2807	27.675
CTD_76	DIEL01	19-May-04	14:31:47	22.3812	27.6728
CTD_77	DIEL02	19-May-04	18:04:04	22.3805	27.6682
CTD_78	IM5	20-May-04	04:04:05	22.2663	27.6418
CTD_79	DIEL03	20-May-04	05:58:40	22.2563	27.6448
CTD_80	DIEL04	20-May-04	07:59:56	22.2507	27.6415
CTD_81	DIEL05	20-May-04	10:13:07	22.2397	27.6408
CTD_82	DIEL06	20-May-04	13:53:31	22.2167	27.6767
CTD_83	DIEL07	20-May-04	15:57:46	22.2115	27.6773
CTD_84	DIEL08	20-May-04	17:56:49	22.2095	27.676
CTD_85	DIEL09	20-May-04	20:00:43	22.2103	27.6795
CTD_86	DIEL10	20-May-04	22:02:59	22.2037	27.685
CTD_87	DIEL11	21-May-04	00:00:48	22.1973	27.6935
CTD_88	TB09IN	21-May-04	03:59:36	22.2205	27.6692
CTD_89	IM6	21-May-04	06:56:06	22.2113	27.6708
CTD_90	TB10IN	21-May-04	11:28:43	22.2098	27.6747
CTD_91	TB11OUT	21-May-04	15:40:24	22.2837	27.6873
CTD_92	TB12IN	22-May-04	07:02:07	22.0605	27.7
CTD_93	TB13OUT	22-May-04	11:27:03	22.0545	27.7867