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GAS EXCHANGE, TIDAL DISPERSION AND BIOGENIC VOLATILES IN THE SOUTHERN NORTH SEA

Compiled by

Andrew Watson, Jane Robertson, Giovanni Daneri and Gillian Malin

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OBJECTIVES:

1) To measure the rate of gas transfer across the sea surface as a function of wind and sea conditions by the release of volatile tracers into the water column.

2) To investigate rates of dispersion and advection due to tidal and residual currents by means of the same tracer release.

3) To investigate the biological sources of oxygen, carbon dioxide, methane and dimethyl sulphide in the coherent body of water marked by the tracers, with a view to obtaining budgets of these gases.

INTRODUCTION

The last cruise of the North Sea programme was a process study involving release of the deliberate tracers sulphur hexafluoride (SF_6) and helium-3 in order to measure gas exchange rates across the sea surface, and simultaneously collect data on the rates of dispersion caused by tidally induced shear in the energetic environment of the Southern North Sea. At the same time dissolved gases having biological sources and sinks were measured both in areal surveys and while on station over 24- hour intervals, in order to build up an accurate picture of their rates of production and consumption. Combining these activities with the tracer release and budgeting provided a unique opportunity to make these measurements against a well-defined reference. (As our experiments have shown, even the drifting buoys used in the North Sea project, which have very low windage, do not move entirely with the water column however well they are drogued.) This was the second time that a tracer release experiment had been performed, but the first time that both release and measurement were successfully accomplished from the same ship without serious cross-contamination. The first experiment was on Challenger cruise 48 in March this year. We benefitted from that earlier cruise in that most of the technical problems had been ironed out and the operations went nearly flawlessly.

EQUIPMENT DEPLOYED AND RECOVERED.

a) A Meteorological buoy, deployed at 52°29'N, 3°46'E , on 7/10/89 at 0530.

b) A Waverider buoy, deployed at 52°29'N, 3°41'E on 7/10/89 at 0618.

c) One ETA mooring carrying two S4 current meters, deployed at 52°25.97'N, 3°47.94'E on 9/10/89 at 1806. This rig was found to be missing on 14/10 at 0615 when we went to check it. The current meters and subsurface buoy were subsequently washed up on the Dutch coast and returned to POL.

d) A dahn buoy moored to a tank on the seabed, deployed at 52°32.4'N, 3°15'E on 8/10/89 at 1930.

e) four "IDB" drogued drifting buoys tracked by Argos satellite and direction finding radio transmitter, initially deployed as follows,
buoy 5: 52°23.19'N, 3°23.56'E on 8/10/89 at 1105
buoy 9: 52°23.68'N, 3°31.77'E on 8/10/89 at 1400
buoy 6: 52°23.82'N, 3°32.88'E on 8/10/89 at 1705
buoy 8: 52°17.2'N, 3°29.8'E on 11/10/89 at 0800

Losses:

The loss of the ETA rig was unfortunate, though we were glad to hear that the current meters were found on the Dutch coast. The use of such a rig, which included a 75m length of rope to tether the flotation carrying the current meters to a subsurface mooring, and which therefore presented a large target to shipping traffic, must be considered a high risk in this region of heavy shipping.

Buoy 5 stopped transmitting to Argos about 24 hours after launching. We spent about 4 hours steaming a search pattern for buoy 5 between 1900 and 2300 on 10/10/89, but without success, so we were forced to consider it lost.

DESCRIPTION OF SUB-PROJECTS.

A) GAS EXCHANGE AND TIDAL DISPERSION BY TRACER RELEASE

Introduction:

In order to calculate the rate at which a gas such as CO_2 or dimethyl sulphide is emitted from, or absorbed by, the sea it is necessary to know the gas exchange rate, K_v. This parameter is known to have a strong dependence on the wind speed and state of the sea. It can be measured in wind tunnels, but the results are dependent on the geometry of the particular tunnel used, and it is impossible to adequately simulate a rough sea in even the largest such facilities. A technique for measuring K_v at sea by budgeting the natural background of radon in the surface has been used for many years; however the results must be integrated over long time periods and are subject to large uncertainties because of inhomogeneities in the sources and sinks of radon.

The method used to measure gas exchange on this cruise involved the simultaneous release of the two gaseous tracers sulphur hexafluoride (SF_6) and helium-3 into the water column and subsequent monitoring of their concentrations. (Both these substances are inert, non-toxic and non-radiogenic gases.) They have vastly different molecular weights and hence exchange to the atmosphere at very different rates, the ratio of which is nearly constant though the absolute value is variable with wind conditions. The change in their ratio with time can therefore be used to deduce the gas exchange rates. Theoretically the measurement is much more controlled than is the radon deficit technique, and can provide accurate measurements over short times. To realise its full potential, a shallow and well-mixed water column is desirable, hence the choice of the SE. North sea as the study site.

A second method of determining the gas exchange rate comes from attempting to "budget" one of the tracers, and thus monitor the total amount in the water and its rate of change with time. This is impractical for helium-3 which was not analysed on board, but was possible for SF_6, because we had built an apparatus which determines SF_6 concentrations in nearly real time from an over-the-side pump. Budgeting the tracer involved surveying the patch by steaming in a grid-like pattern while analysing surface water for SF_6 with this instrument.

A different type of information can also be recovered from these surveys: tracer releases have in the past been used to document water advection and dispersion due to tidal and wind forcing. normally a fluorescent substance such as rhodamine is used for this purpose. However, a very large release of rhodamine would be required to follow the dispersion of tracer for times in excess of a week. The SF_6 tracer release will allow a relatively long-period estimate of dispersion due to the tide.

This was the second experiment to try out the new tracer technique, the first having been Challenger 48 earlier in the North sea project. It was however the first cruise on which both release of the tracer and its measurement were conducted from the same vessel: on the earlier cruise the MAFF vessel *Corystes* was used for the release. In order to accomplish the release with the minimum of cross contamination of the ship, a large (1000 litre) tank full of salt water with the two tracers dissolved in it was prepared just prior to the cruise, in the yard at Escombe Lambert shipping agents in Gt. Yarmouth. The tracers were dissolved into the water by continuously bubbling them around in a nearly closed circuit: in the case of SF_6, which is inexpensive, a continuous bleed of SF_6 through the circuit was introduced in order to strip out the atmospheric gases which were initially dissolved in the water. In the case of helium -3 which was added after the SF_6 and which costs £400 per gaseous litre, the circuit was kept rigorously closed. After addition of the tracers, the tank remained sealed until deployment, so that no contamination of the ship should occur which would make subsequent measurement of low concentrations difficult. Measurements of the concentrations of the gases in the tank were made using a gas chromatograph equipped with a thermal conductivity detector installed at the agents office.

Release: to release the tracers, a header tank was set up above the level of the top of the tank, and was connected to the input hose of the main tank. The output was led out via a flowmeter to a hose, the end of which was deployed over the stern to a depth of 10 metres. Water from a deck hose was fed to the header tank, and from here displaced water in the main tank through the output hose. The flowrate was adjusted by a stopcock and was increased steadily throughout the deployment period to compensate for the steady drop in concentration of the tracers in the tank. This complex release procedure was followed in order that the tracer should not be exposed to the atmosphere before release, which would have resulted in contamination and a non-constant initial ratio of helium-3 to SF_6.

Measurement: at six times subsequent to the tracer release, CTD/multisampler casts were made to determine helium-3/SF_6 ratios. Generally, 4 samples for SF_6 and one for helium were taken from each of 3 depths (2, 10 and 25m). The SF_6 samples were analysed within a few hours of sampling, while the helium samples were stored for analysis post-cruise.

Four complete surveys of the tracer patch were completed, each lasting on the order of 24 hours. During these, surface water obtained using an overside pump was passed continuously through an automated purge and trap system attached to the gas chromatograph. Cryotrapped samples were analysed for SF_6 every 3 minutes, with the results being transmitted to the computing system for display in the plot. Due to the delay in the pumping and purge and trap systems, concentrations were plotted about 7 minutes behind real time. In order to increase the spatial resolution of the surveys, the ship steamed at 7-8 Kts, somewhat below full speed. Figs 1-4 show the "liveplot" tracks produced by the four surveys. These differ substantially from the actual ship's tracks over the ground, being approximations to the ships movement through the water.

B) OXYGEN PRODUCTIVITY

The object of these measurements was to measure the diurnal cycle of productivity in a well-characterised body of water, over a period of many days. The measurements will enable us to correlate changes in algal biomass with changes in productivity as measured both by oxygen and C-14 techniques. The degree of supersaturation of oxygen in the water is a function also of the gas exchange to the atmosphere. We will be able to account for this accurately as it is being measured measured by the tracer experiment.

Discrete samples of dissolved oxygen from 3 depths were taken from a total of 44 CTD casts in a coherent body of water marked out by the SF_6 tracer patch and drifting buoys. The oxygen was chemically fixed and determined colourimetrically using an automatic endpoint detector.

Oxygen and C-14 incubations were performed on deck during four 24 hour cycles. In the first two the light bottles were incubated at 5 simulated light depths for 12 hours. In the second two the light bottles were incubated at surface light intensity and fixed every three hours. Biomass measurements (chlorophyll and cell numbers) were taken from all the CTD casts. Changes in biomass from the on-deck incubations were also monitored.

C) CONTINUOUS AND DISCRETE MEASUREMENTS OF PCO_2 AND CH4

An automated gas chromatographic technique for both continuous and discrete measurement of pCO2 and CH4 was employed throughout the cruise. The technique operated well under all conditions and demonstrated a precision of c. 0.5% over most sections of the cruise.

Continuous values of pCO2 and CH4 were obtained via an on-deck equilibrator and header tank linked to the ships non-toxic seawater supply. Two seawater values, one standard and one marine air value were recorded half hourly. The continuous measurement was divided into two sections:

1) Three survey periods of approximately 24h duration in the area of the SF6 'patch'. During these mapping sections pCO2 was close to air equilibrium or slightly undersaturated by typically 5%. CH4 was always observed to be supersaturated in the surface waters by 7-16%. These survey sections provide the first mapped, directly measured pCO2 values in the North Sea.

2) During the first three 24 h periods during which oxygen productivity was measured, pCO2 was recorded continuously with the ship maintaining position close to a buoy and

drogue. The aim was to record pCO_2 values in the water column along with oxygen concentrations in order to compare any diurnal change in the relative concentrations of the two gases. Further calibration and correction for temperature effects is necessary before an estimate of in situ net community production by pCO_2 change is possible.

3) A survey section of 19h duration was carried out close to the outflow of the River Rhine. Supersaturation of CH_4 was observed to increase from 16 to 88% with initial comparisons suggesting a rise in CH_4 concentration corresponding to a drop in salinity. In contrast to the region being mapped for the dispersion of SF_6 pCO_2 was supersaturated by between 5-15% during the survey.

In addition to continous measurement of surface water a newly developed system for providing discrete pCO_2 values was tested during the cruise. A good comparison was obtained between water sampled continuously from the non-toxic and compatible water obtained using the CTD.

A number of on-deck incubations were carried out measuring the change in pCO_2 observed in the light and dark, concurrent with the series of oxygen incubations. Initial calculations suggest a reasonable correlation between the change in concentration in the two gases. Further calibration and calculation is necessary before a more thorough comparison can be carried out, but it is hoped to calculate a series of photosynthetic and respiratory quotients for the incubations. All on-deck incubations coincided with a series of 2 hourly CTD casts for oxygen. In addition to the on-deck incubations, one series of 2 hourly CTD casts for a 24 h period was measured for discrete pCO_2.

Further development and refinement is necessary to the discrete system for measuring pCO_2, however, initial results are encouraging and the system worked well under all conditions.

D) DMS AND DMSP PRODUCTION

Surface seawater samples were taken using both the CTD/rosette and the underway pump at intervals throughout the cruise. Dimethyl sulphide (DMS) was extracted amd concentrated using a cryogenic purge and trap technique and analysed using a gas chromatograph with flame photometric detector. Concentrations of dimethyl sulphoniopropionate (DMSP), the cellular precursor of DMS, were also measured. Samples were taken for onshore chlorophyll analysis and phytoplankton identification and enumeration. Approximately 60 samples were analysed for DMS. The observed concentrations fell in the range 15-25 ng S l^{-1}, which represents relatively low values. We sampled over of the 24 hour oxygen productivity experiments, but the results do not show any obvious diel cycles in DMS or DMSP concentration. It should be possible to use the DMS data to calculate the air-sea exchange flux of this gas once the gas transfer co-efficient for the study area is known from the tracer experiment.

As part of an onging study into the effects of sample handling on measured DMS/DMSP concentrations, some of the samples were analysed before and after filtration through millipore AP25 depth filters. Finally, in addition to the normal DMS/DMSP samples, filter-fractionated seawater was used in two sets of of experimental incubations (90 analyses in all) to assess the level of bacterial breakdown of DMSP.

CONDENSED LOG OF ACTIVITIES

6/10 1500 Departed from Gt. Yarmouth.

1650 Resumed passage following an incident in which we had to return to Gt. Yarmouth to disembark one of the ship's personnel.

7/1C 0030 Arrived at prospective study site, 52°20'N, 3°20'E. CTD station 2863 to determine water structure, samples for O2, nutrients, DMS.

Steamed to site for deployment of buoys.

0545 Deployed Met buoy at 52°29'N, 3°46'E.

0618 Deployed Wave rider at 52°29'N, 3°41'E.

0830 Returned to prospective tracer release site. Weather worsened and it was decided that it was too rough to begin the tracer deployment. We therefore made a survey of the area to determine relative levels of biological activity in the water by fluorometer. Comparatively high levels were found for this time of year, and quite widely distributed.

2100 Having completed the survey, it remaining too rough to deploy any equipment, we remained hove to near 52°20'N, 3°20'E.

8/10 1000 The weather having moderated we commenced deployment of the tracer from the 1000-litre tank, at position 52°23'N, 3°29'E. The deployment was spread over the 6-hr. period during which the tide was running to the south-west, during which time Challenger remained hove to facing the North- Westerly wind. This arrangement ensured that any tracer released into either the atmosphere or the sea was carried away from the ship. Argos buoys were released at the start, after three hours and after 6 hours.

1930 After finishing the deployment we steamed to a position about 20 nm from the deployment site and temporarily disposed of the tank which had contained the tracer on the sea bed, marking the tank with a dahn buoy. This was done to minimise the possibility that the ship would be contaminated by tracer still remaining in the tank, making it impossible to make low-level measurements.

9/10 0030 Returning to the study site we were quickly able to pick up the presence of the tracer in the water using the instrumentation on the ship. No contamination from the deployment was seen at any time during this part of the operation or at any other time, confirming that our deployment method was completely "clean". This was a major technical achievement considering that the measurement equipment was sensitive to the contents of the tank after dilution by a factor of 10^{16}, and was sited within about 10 yards of the tank during the deployment.

CTD and samples were taken for SF_6 and ^3He, to provide the initial condition for the gas exchange experiment.

SF_6 samples were analysed during 0100-0600

0700 Commenced the first of our series of 24 diel productivity/volatiles measurements. During these periods the ship remained close to a drogued buoy near the centre of the tracer patch. CTD/water bottle samples were taken at regular intervals for periods of 24 hours. Samples were taken for O2 productivity, Chlorophyll, and DMS/DMSP. O2, pCO_2 and methane were monitored continuously in the surface water. CTD stations were taken at 0700, 1000, 1300, 1600, 2200, 0000, 0200, 0400 and 0600

9/10 1800 We steamed away a short distance to 52°26'N 3°48'E and deployed the ETA current meter rig.

10/10 0800 Commenced first tracer survey. The ship steamed a grid-like pattern while underway measurements of SF_6 were made. A "liveplot" diagram, showing the position of the ship relative to the water by dead-reckoning using the EM-log and gyro outputs, was displayed in the plot. Tracer concentrations were marked on this diagram in near real time, and the diagram was used to guide the ship while making the survey. The liveplot also provided an approximate picture of the patch, though because of inaccuracies in the EM logs it will be necessary to rework the data using decca positions of the ship and the buoys to get an accurate picture.

1900 Began a search for drifting buoy 5 which had ceased transmitting its position after 1642 on 9/10. We searched unsuccessfully until 2300.

11/10 0000 CTD 2878, samples for helium and SF_6 at study site.

0600 We began the second diel series of measurements. CTDs at 0600, 0900, 1200, 1500, 1800, 2300, 0100, 0300, 0500. Measurements as on 9/10. This series was made in the centre of the patch, the previous survey having shown that Argos buoy 9 was separating from the patch. At 0800, argos buoy 8 was launched in the centre of the tracer to provide a reference point for the ship.

12/10 0545 Before beginning the next patch survey, Argos buoy 8 was recovered, fitted with a second drogue, and re-deployed in the centre of the patch again. This was done because it became clear during the previous diel experiment that the buoy was slipping downwind of the tracer. We felt that doubling the drogue size would minimise this effect.

1000 Commenced tracer patch survey no. 2.

13/10 0100 CTD station 2889 for helium and SF_6 samples. Analyses completed during night.

0600 Commenced diel experiment 3 with CTDs at 0600, 0900, 1200, 1500, 1800, 2100, 2300, 0200, 0500. During the night the light on buoy 8, being used for reference, failed to come on.

14/10 0615 We steamed to the position of the ETA rig in order to service the current meters. The rig was gone. Wave rider and Met buoy checked and found to be OK.

1030 New light put on argos buoy 8.

1100 Commenced tracer survey 3.

1930 An electrical short circuit caused all the computers on the ship to crash. Survey recommenced about 2300.

15/10 0730 CTD 2899 in centre of patch for Helium, also the start of diel experiment 4.

0830 Because of the recurrent problem of the buoys, even the double-drogued buoy 8, slipping downwind of the patch, we picked up buoy 6 which was now some 6 miles away and redeployed it in the centre of the patch, using it as a reference for this series of CTDs.

CTDs at 1118, 1300, 1500, 1800, 2100, 2300, 0200, 0500.

0520 We began a 24 hour moving survey of the region to the south and east, seaward of the Rhine/Scheldt estuary. SInce to our knowledge this was the first time that pCO_2 and methane measurements have been made in a survey mode in the North sea, and since we had consistently observed methane levels above saturation with the atmosphere, we were curious to see what influence if any the Rhine waters have on the levels of these volatiles. In the event, though we did not encounter very low salinities which would signify a heavy Rhine influence (minimum salinities of 33.0 PSU, corresponding to about 7% fresh water) these correlated with methane levels up to twice saturation level, indicating a substantial source to the atmosphere due to the influence of the Rhine. Whether this is due to in-situ biological activity or is entirely advected from the Rhine we cannot at present say. pCO_2 levels inversely correlated with the methane.

17/10 0000 Returning to study site, we searched for the tracer.

0200 Tracer having been contacted, made CTD 2908 in centre of patch for SF_6, helium-3 analyses.

0250 Conmmenced tracer survey no. 4

0845 Survey interrupted for CTD to collect water for on-deck incubation.

1720 Wave rider recovered

2300 End of tracer survey, CTD no. 2910 for SF_6, helium-3.

18/10 0030 Recovery of buoys 8 and 6. During the recovery of buoy 8 the lower drogue that we had added became ensnared in the ship's propeller, resulting in loss of the drogue but without harm to the ship it would appear.

0230 Recovery of buoy 9. Commenced steaming to position of tank deployment, 52°32.4'N, 3°15'E.

0600 Last tracer analyses were completed.

0700 Recovered tank from seabed, in good condition. Set course for Gt. Yarmouth.

1800 Docked at South Quay, Gt. Yarmouth.

STATION LIST

The following variables derived from the CTD package were recorded at all stations: temperature, salinity, fluorescence, transmissivity, fluoresence, oxygen electrode, upwelling irradiance, downwelling irradiance.

Letter codes: On biological productivity stations, O2 by Winkler, chlorophyll "a" by fluoresence and nutrients (niitrate, nitrite, silicate, phosphate) were measured. These are indicated below by code "B". On some stations discrete pCO2 was measured: these are indicated by "C". Stations for tracers (helium-3 and SF_6) are indicated by "T".

At all stations, water samples were taken at 2, 10, and 25 m.

DATE	TIME	LAT(N)	LONG (E)	STN NO.	CODES
7/10	0028	52°19.7	3°20.2	2863	B,C
	1126	52°22.5	3°15.5	2864	B,T,C
8/10	2144	52°23.7	3°31.6	2865	B,C
	2233	52°23.9	3°32.0	2866	B
9/10	0030	52°23.3	3°31.5	2867	B,T,C
	0707	52°19.7	3°29.9	2868	B
	1005	52°21.3	3°31.8	2869	B
	1304	52°21.3	3°32.0	2870	B
	1601	52°19.5	3°30.2	2871	B
	2023	52°18.3	3°30.6	2872	B
	2217	52°19.6	3°31.1	2873	B
10/10	0005	52°20.1	3°31.9	2874	B
	0202	52°19.9	3°30.6	2875	B
	0402	52°18.3	3°30.0	2876	B
	0559	52°17.1	3°28.6	2877	B
	2354	52°19.5	3°30.5	2878	T
11/10	0602	52°18.6	3°28.4	2879	B
	0903	52°17.3	3°29.6	2880	B
	1200	52°19.3	3°32.5	2881	B
	1501	52°21.3	3°33.0	2882	B
	1803	52°19.5	3°31.6	2883	B
	2104	52°17.1	3°29.7	2884	B
	2302	52°18.2	3°31.2	2885	B
12/10	0102	52°20.4	3°34.0	2886	B
	0302	52°22.0	3°34.8	2887	B
	0502	52°21.3	3°34.3	2888	B
13/10	0111	52°21.4	3°33.3	2889	T
	0603	52°22.3	3°34.1	2890	B
	0904	52°19.1	3°31.4	2891	B
	1202	52°19.5	3°32.2	2892	B
	1506	52°23.4	3°34.8	2893	B
	1802	52°23.5	3°35.6	2894	B
	2121	52°20.0	3°30.6	2895	B
	2304	52°19.0	3°28.1	2896	B

DATE	TIME	LAT(N)	LONG (E)	STN NO.	CODES
14/10	0220	52°22.6	3°34.5	2897	B
	0501	52°24.1	3°36.0	2898	B
15/10	0719	52°22.3	3°33.4	2899	T,B,C
	1119	52°18.8	3°31.3	2900	B,C
	1303	52°19.5	3°32.3	2901	B,C
	1503	52°22.7	3°34.8	2902	B,C
	1802	52°25.8	3°36.6	2903	B,C
	2102	52°22.9	3°35.6	2904	B,C
	2302	52°20.9	3°33.3	2905	B,C
16/10	0203	52°21.7	3°34.7	2906	B,C
	0502	52°25.8	3°35.0	2907	B
17/10	0208	52°21.8	3°32.9	2908	T
	0844	52°26.6	3°38.3	2909	B
	2204	52°26.0	3°36.4	2910	T

POINT FOR THE ATTENTION OF RVS

EM LOG: This appears to be inaccurate, at least in the port-starboard component which reads persistently about 0.3 Kt to port under virtually all circumstances. This impacted our experiment in that the "liveplot" of tracer concentrations was inaccurate. In other respects this cruise went very well and there were virtually no other technical problems.

ACKNOWLEDGEMENT

The science party would like to record their appreciative thanks to the officers and crew of *Challenger* for helping to make this a successful cruise.