INVESTIGATING METAL TRANSPORT IN SUSPENDED PARTICULATES FROM THE NORTH-EAST ENGLISH COAST TO THE DOGGER BANK

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Background

Surveys performed over the last decade [1, 2] have shown some elevated concentrations of certain metals, e.g. cadmium and chromium, in the predominantly sandy sediments of the Dogger Bank. These are unexpected because sands are not usually considered to readily accumulate contaminants. The Tyne/Tees region also has elevated concentrations of these metals in its sediments. This has led to speculation that metals in the offshore region originated from the coastal zone. However, it is only recently that direct evidence for a well defined and persistent pathway has been demonstrated.

Brown *et al.* [3] described a spring/summer jet-like flow extending continuously for at least 500 km along the ~40-50 m contour from the Firth of Forth, passing eastwards to the north of Flamborough Head and skirting the northern flank of the Dogger Bank. The circulation is associated with strong temperature gradients at the margins of a deep pool of cold dense winter water isolated below the summer thermocline. We are investigating whether there is evidence that the mechanism transports particulate contaminants to the Dogger.

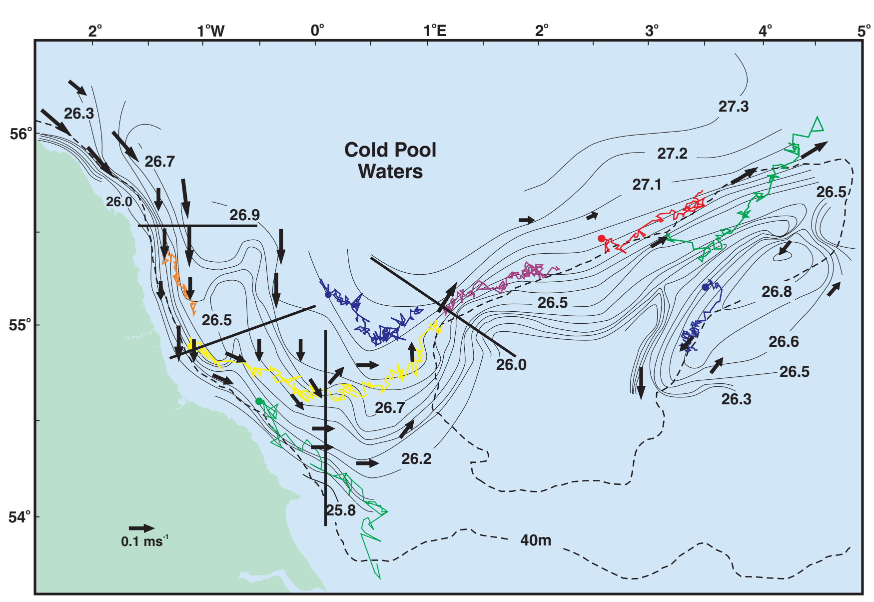

Figure 1. 1998 CTD transects superimposed on drifter tracks and bottom density off the Tyne/Tees

Figure 1 shows the 1997 trajectories of satellite-tracked drifters, drogued at 30m, superimposed on contours of bottom density. Tracks follow the spatial structure of density/bottom fronts (rather than bathymetry), which represents a contour map for residual flow. Included is a synthesis of flow (➔) derived from geostrophic estimates calculated normal to each section. Solid lines indicate the location of CTD/Scanfish transects undertaken during 1998 to define the temperature, salinity, density, fluorescence and turbidity fields.

Methods

Figure 2 shows density and estimates of geostrophic velocity derived for the section orientated north-south. Peak flows (eastward) associated with the bottom fronts were seen at ~42 km and between 70-100 km. Such data were used to select the locations of CTD stations, with water bottle samples taken to determine nutrients, chlorophyll and suspended material. Samples were generally collected at three depths: ~6 m below the surface ("surface"), at the thermocline ("middle" - usually 20-30 m depth), and ~6 m from the bottom ("bottom"). Where there was no stratification, samples were collected at surface and bottom.

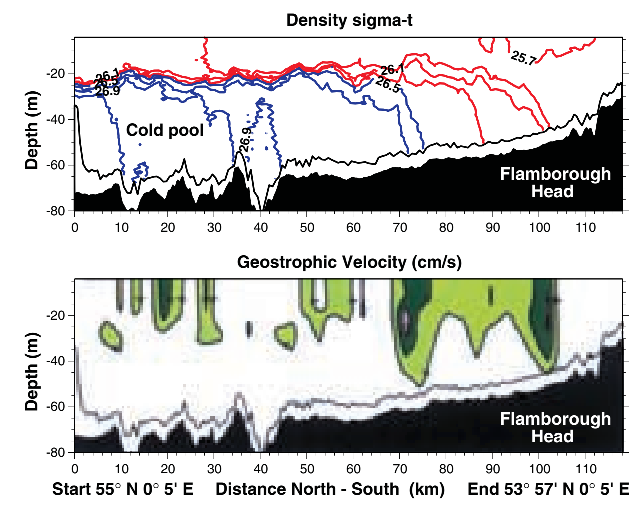

Figure 2. Density and geostrophic velocity of north-south transit.

Metals analysis

100 l seawater was filtered through 293 mm acid-washed and DI-rinsed cellulose nitrate 0.45 µm filters. Filters were rinsed with DI to remove salt then stored in self-sealing bags. Subsequently, filters were pre-digested in conc. nitric acid on a hotplate. The mixture was then subjected to HF/HNO_3 digestion, followed by addition of boric acid. Metals analyses were performed by ICP-MS (Cd, Cr, Pb, Li, Rb) and AAS (Al).

Quality control

Field filter blanks were performed by recycling 25 l deionised water through a filter for 20-25 mins whilst at sea, before, during and after sampling transects. Results presented here have been blank-corrected for both field and analytical blanks. Table 1 shows field blank data (n = 12) : those for Cr are higher than would be desired, but because of their interest to the Tyne/Tees and Dogger regions, we have continued to study them.

Reproducibility of the entire sampling and analytical procedure was estimated from the pairs of samples taken from the same CTD dip (table 1). Variability in Li results may be attributed to low concentrations, but those for Cr are mainly caused by variability in the blanks.

Certified reference materials (CRM's) were taken through both digestion procedures (table 2), showing that metals analyses were generally accurate and reproducible. Data for Cr were significantly lower than the certified value - probably caused by the difficulties in digestion of this element. In general, the total digestion was satisfactory, as evidenced by data for matrix elements such as Al, Li and Rb.

Table 1. Field filter blanks and sample reproducibility

Filter blanks	Al mg	Cd µg	Cr µg	Pb µg	Li µg	Rb µg
Mean	0.064	0.002	3.308	0.315	0.022	0.018
95% CI	0.038	0.002	0.527	0.070	0.028	0.025
Sample Reproducibility	**Al%**	**Cd%**	**Cr%**	**Pb%**	**Li%**	**Rb%**
95% CI	3.0	10.0	27.3	13.0	21.8	13.8

Note CI = confidence interval
Sample reproducibility calculated from 4 pairs of 100 litre samples

Table 2. Recoveries from certified reference material BCSS-1

BCSS	Al	Cd	Cr	Pb	Li	Rb
Mean % recovery	98.3	103.9	76.0	96.3	99.4	100.8
95% CI	3.4	6.7	3.6	3.8	2.7	3.0
N	40	45	40	40	40	40

Results

Data are presented for two transects: one running north south from the Tyne/Tees to the Flamborough Head, and one running into the north western Dogger Bank. Data have been reported as absolute concentrations, i.e. µg per 100 l water sampled.

Examples of metal concentrations and ratios are presented in Figs 3a-f. Data for lead and chromium were normalised to an analogue for the clay content such as aluminium or rubidium (table 3). Low concentrations of Li led to some detection problems.

Surface and middle samples might be expected to contain low amounts of clays relative to bottom, so data were checked to ensure that regressions were not biased depending upon depth. In general, data were randomly spread, suggesting no bias. However, for lead in bottom sediments from the NW Dogger transect, there were positive residuals (against Al and Rb) for those samples collected off the Bank.

Data for cadmium on the suspended load are normalised to chlorophyll, since this component provided a good normaliser for Cd (table 3) while those for clays did not. Recent research has indicated relationships between cadmium and phytoplankton [4, 5].

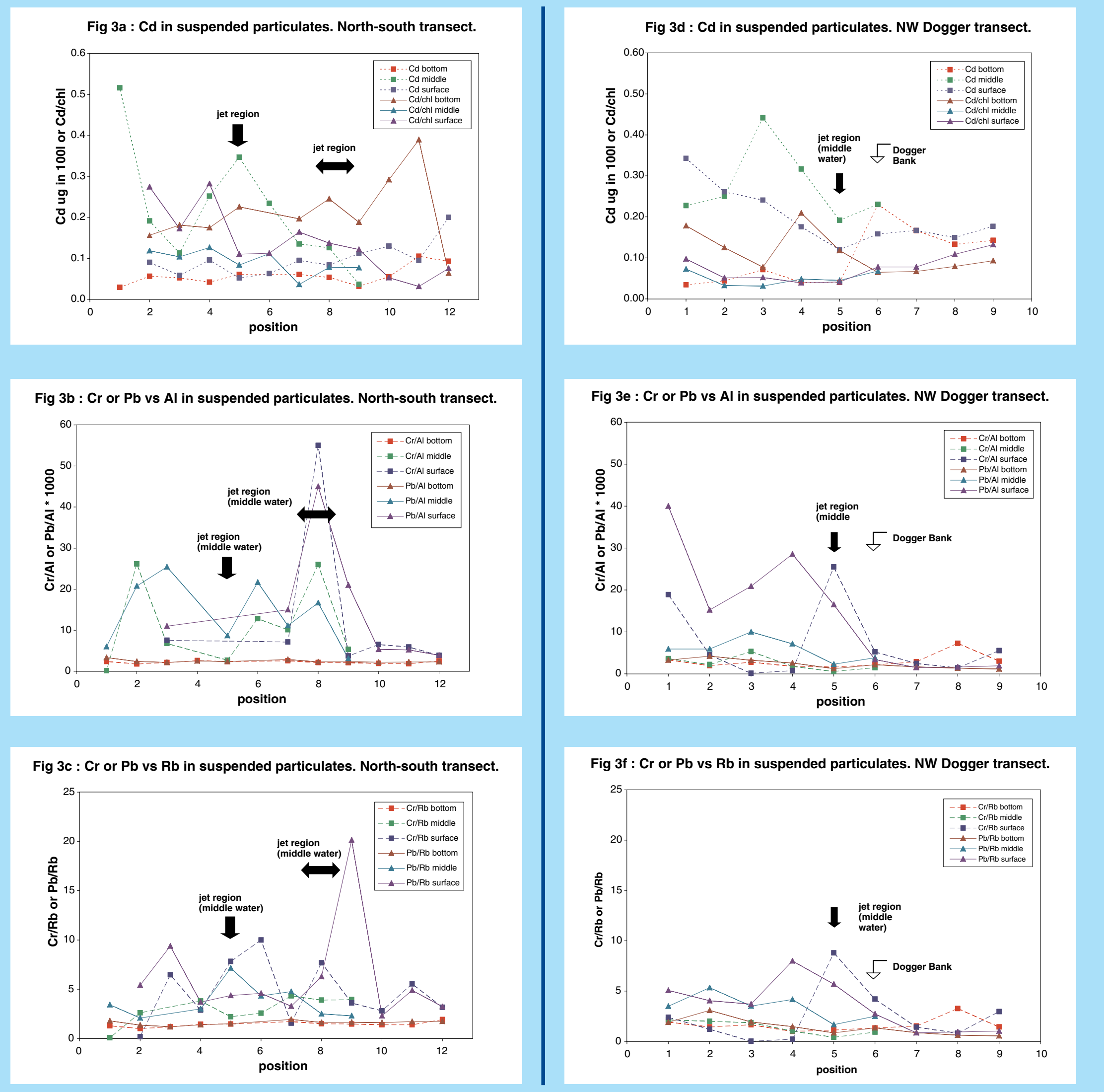

Table 3. Regression data for metal : normaliser

Transect	Metal: Normaliser	r²	v	Transect	Metal: Normaliser	r²	v
North-south	Pb : Al	0.957	25	NW Dogger	Pb : Al	0.491	23
	Cr : Al	0.938	25		Cr : Al	0.701	22
	Pb : Rb	0.93	29		Pb : Rb	0.568	21
	Cr : Rb	0.921	29		Cr : Rb	0.811	20
	Cd : chl	0.783	30		Cd : chl	0.738	23

P all < 0.001
chl = chlorophyll a

Discussion

We are looking to see if there is any evidence for the transport of contaminants from the Tyne/Tees region to the Dogger Bank - particularly with respect to Cr and Cd as they are elevated in these coastal sediments [1]. Lead has also been examined to provide a comparison between Cr and another lithogenic metal.

Test 1 = are absolute concentrations different/higher in the jet region? i.e. can we find evidence for the density-driven circulation transporting contaminated material offshore? However, examining the absolute concentration alone may provide ambiguous results if suspended loads are very variable between sample points. We may just be measuring differences between high-clay and low-clay containing samples - which may not be related to the transport mechanism of interest.

Test 2 = do there appear to be differences between normalised metal concentrations in the jet region compared to elsewhere? This would alleviate problems caused by suspended load in (1), but if material across the transect is all from same source, we won't see any differences.

Maxima and minima in absolute concentrations and in those normalised to Al, Rb and Li were assessed against the areas where the greatest transport potential in the jet region was expected. This was at #5 for the northwest Dogger transect, and at #5 and #8 for the north-south transect. This approach simplified the data considerably; while detail was lost, it provided an initial sift for gross effects.

In the jet zone for both transects cadmium concentrations showed a minimum or were comparable to surrounding waters. Only one peak in absolute concentration was observed - at #5 in the north-south transect, and this was not replicated at #8. Normalised values either showed a minimum or were within the average data range for that transect.

Normalised chromium was elevated at #8 but not #5 in the middle water of the north-south transect: it was not elevated at the Dogger. Interestingly, these values were elevated in the surface waters above the jet in both transects examined here. The absolute concentration was positive in the bottom sample from the Dogger, but was a minimum or average elsewhere.

Like chromium, the only absolute lead concentration that was positive in the jet region was in the bottom sample from the Dogger transect. Normalised lead values were either minima or equivalent to surrounding waters. A worst case for these tests occurred in the north-south transect; against Al there was a minimum at #5 but a peak at #8, but the reverse when normalised against Rb. Interpreting such data is difficult.

Although evidence for elevated concentrations in the jet zone is hard to find in these data, flux calculations may show whether the seasonal rapid transport of coastally-derived material is significant in offshore areas. Data collected from the Dogger Bank in 1999 may be useful in this respect.

Summary

Overall, cadmium distribution did not appear to be related to the location of the jet. Lead data did not seem correlated with the jet region. Chromium was not elevated in the middle water - where the jet runs - but normalised data appeared elevated in surface waters above the jet. This observation will be explored further in the analysis of other transects.

Further work

Lead isotope ratios are being examined to see if we can characterise the material from the Tyne/Tees region and contaminant fluxes quantified.

Acknowledgements

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