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Metals in Surficial Sediments of the North-West Irish Sea

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Information concerning the status of chemical contamination in the Irish Sea is surprisingly limited given that it is semi-enclosed and the number of human activities that influence the environmental quality (Dickson and Boelens, 1988). Most research has been concentrated on the north-east, where freshwater and industrial discharges from the west coast of Great Britain contribute approximately 80 % of the anthropogenic loading of trace metals to the Irish Sea (Service *et. al.,* 1996). The possibility of contaminants being transported from the eastern Irish Sea to the east coast of Ireland has been inferred by Jefferies *et. al.* (1973) and Burrows (1986), and recent evidence suggests that the summer gyre in the western Irish Sea could act as a retention zone for contaminants (Hill *et. al.,* 1997).

The north-west Irish Sea is an area of oceanographic diversity (Gowen *et. al.,* 1995). The central region stratifies during the summer due to solar heating, weak tides and deep water, and is bound to the north and south by shelf sea tidal mixing fronts (Simpson and Hunter, 1974). There is growing evidence to suggest that two centres of stratification exist during the summer, and that the flow of the summer gyre which dominates the surface circulation regime, closely follows the contours of the vertical stratification parameter 4 (Hill *et. al.,* 1997).

MATERIALS AND METHODS

Sediment samples were collected between 12 and 16 May 1997 at 31 locations in the north-west Irish Sea. Where possible samples were collected by mini-corer, but where the substrate was to too hard or coarse a Day Grab fitted with stainless steel jaws was employed. To ensure sampling artefacts were not introduced by using 2 collection techniques, 3 sediment samples were collected from successive deployments by the grab and mini-core at station 30 and subjected to trace metal analysis. A t-test of two variances showed there was no significant ($P < 0.05$) difference between the two methods.

At each station for heavy metal analysis two samples of approximately 200 g were taken from the surface (0-1 cm) layer of sediment using a polyethylene scoop and stored in a polycarbonate container at -15 °C. On returning to the laboratory one sample was stored in an archive freezer, and the other freeze-dried, sieved at 2 mm

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subsampled and ground to a powder using a mortar and pestle. A further subsample of five hundred milligrams of this powder was totally digested in a microwave oven using a combination of hydrofluoric acid and *aqua regia*. The resulting solutions were analysed by atomic absorption spectrometry for Al, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. Certified reference material (CRM 277) and a blank was analysed with each batch of samples. The analytical precision and accuracy of the certified reference material can be seen in Table 1. Blank concentrations were negligible. Replicate analysis of 4 subsamples of the same sediment sample, and of 4 samples taken from the same station are shown in Table 1.

Organic carbon was measured following flash combustion in a temporary enriched atmosphere of oxygen using a CHN analyser after treatment with sulphurous acid (AERD, 1992). Particle size analysis was conducted by laser granulometry (Mastersizer/E Malvern Instruments), and the results summarised using the graphical methods of Folk (1974).

Table 1. Recovery of the 'total' digestion procedure, related to certified reference material CRM 277; concentration units are µg g^{-1} except Al, Fe and Mn (mg g^{-1}); * indicative concentrations. Results of replicate analysis.

Element	Certified	Found	R.S.D. of 4 subsamples	R.S.D. of 4 Samples
Al*	47.8 ± 1.3	40.5 ± 1.3	1.6	1.4
Cr	192 ± 7	163 ± 12	3.5	4.1
Cu	101.7 ± 1.6	96.5 ± 1.3	1.0	3.5
Fe*	45.5 ± 1.1	39.8 ± 1.6	2.8	2.4
Mn*	1.58 ± 0.04	1.49 ± 0.01	5.7	4.8
Ni	43.4 ± 1.6	36.5 ± 1.1	4.2	5.0
Pb	146 ± 3	126 ± 4	4.3	3.9
Zn	547 ± 12	542 ± 23	0.5	1.5

RESULTS AND DISCUSSION

The results are graphically presented in Figs. 1 and 2. The combined effect of deep water and weak tidal currents indicated by moderately sorted sediments to the west of the Isle of Man allows the deposition of fine grained sediments of which > 90 % was < 63 µm. This area was surrounded by bands of progressively coarser sediments until very poorly sorted sand was reached in the north and south of the study area. Metal distributions mimicked the distribution of % < 63 µm with highest concentrations found in the fine sediments to the west of the Isle of Man, and progressively decreasing concentrations towards the periphery of the study area. Strong correlation exists between the metals and % silt/clay, however no statistically significant correlation is observed between organic carbon and trace metals, inferring that the concentrations of metals are predominantly determined by grain size throughout the whole region. The exceptions to this are those stations

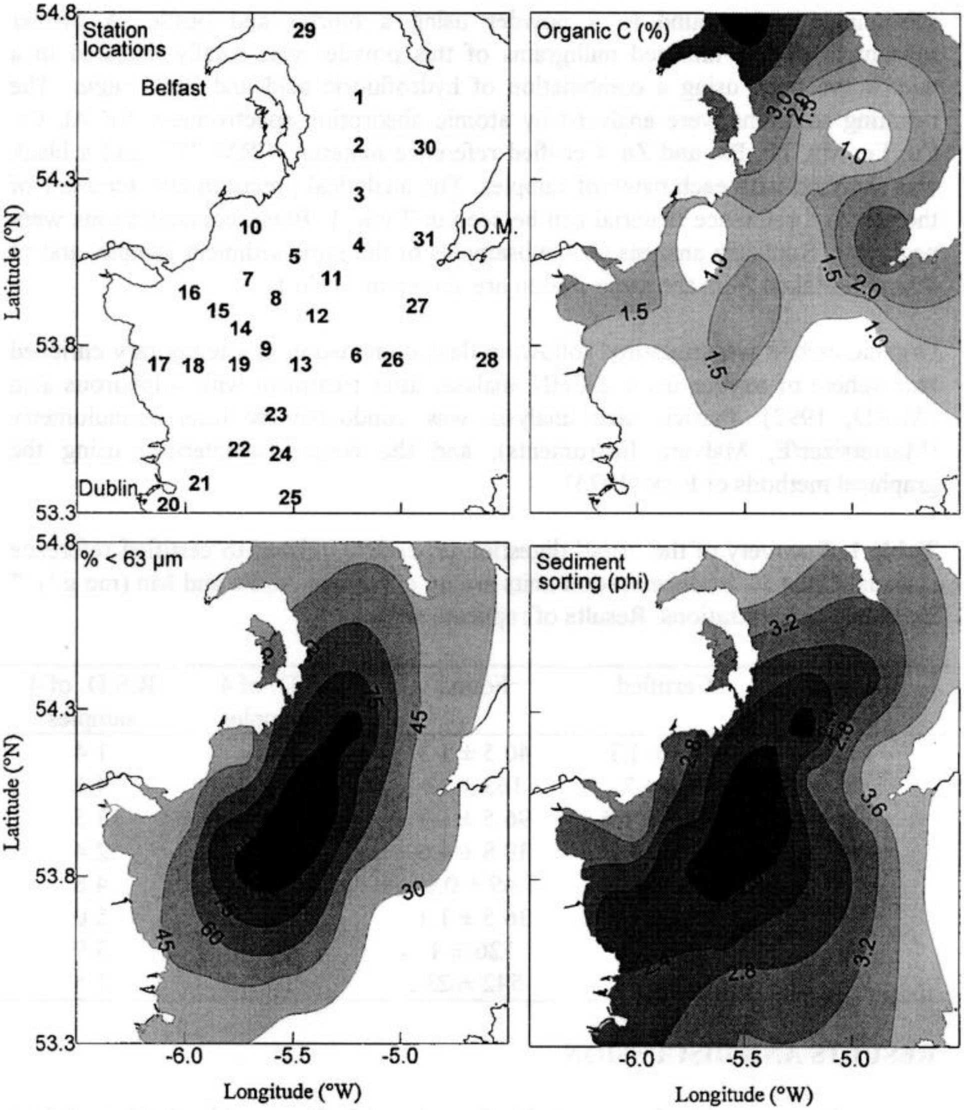

Figure 1. Station locations, and the distribution of C^{org}, and sediment parameters.

under the possible influence of anthropogenic contamination (see below). Chromium, Cu, Ni, Zn and Pb showed two concentration maximums, encompassing station 3, and stations 5, 8, 11 and 12.

To allow further inferences to be made about controls on metal distributions, a geochemical normalisation approach has been employed, utilising Al to compensate for granulometric and mineralogical differences (Fig. 3). Loring (1991) stated that before normalising metal concentrations there must exist a strong relationship between particle size, normaliser, and metal concentrations. From the results Al correlated with % silt/clay ($r = 0.96$, $P = < 0.01$) and all metals correlated ($P < 0.05$) with Al, and so these conditions are satisfied.

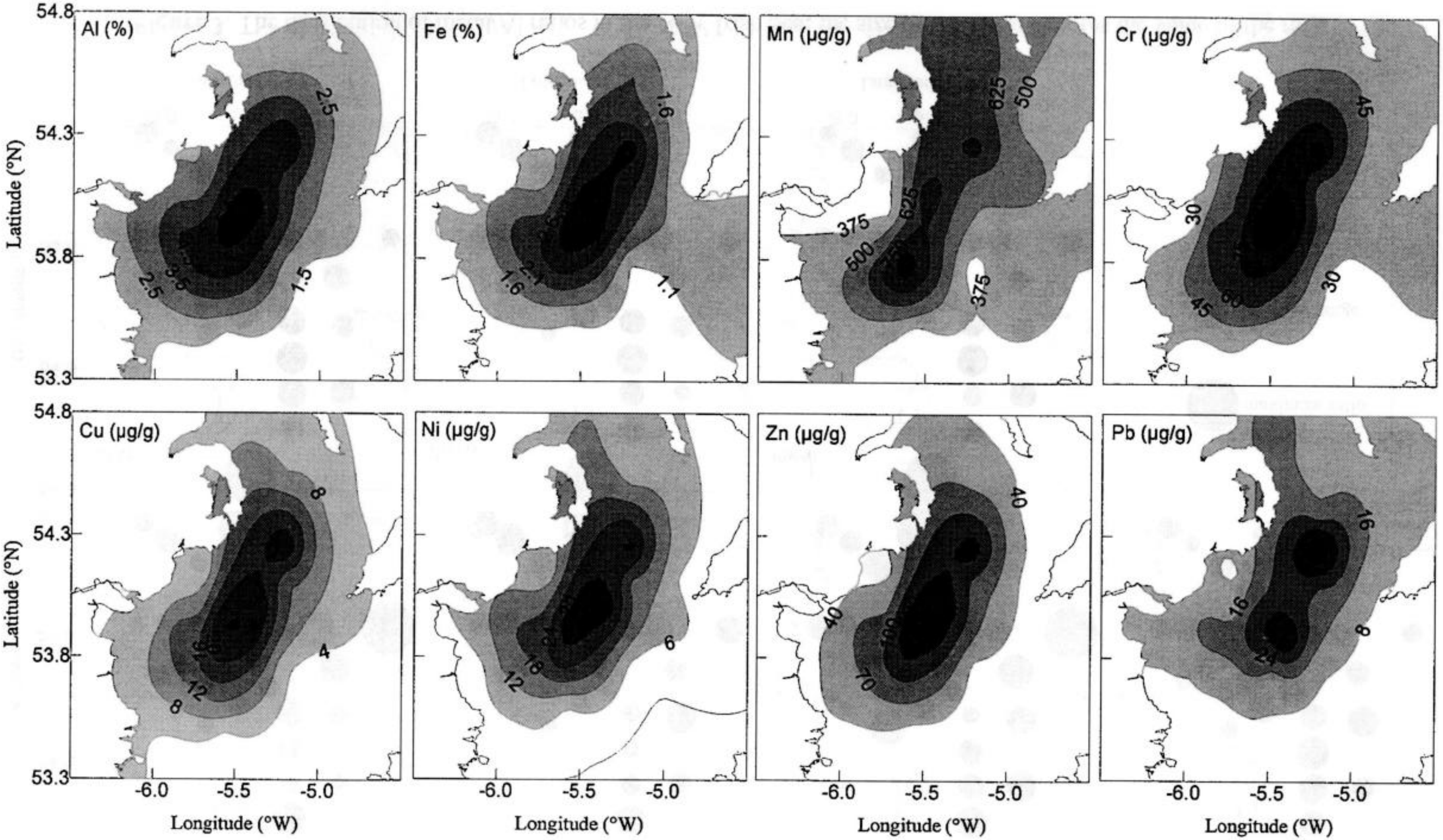

Figure 2. The distribution of trace metals in the N-W Irish Sea

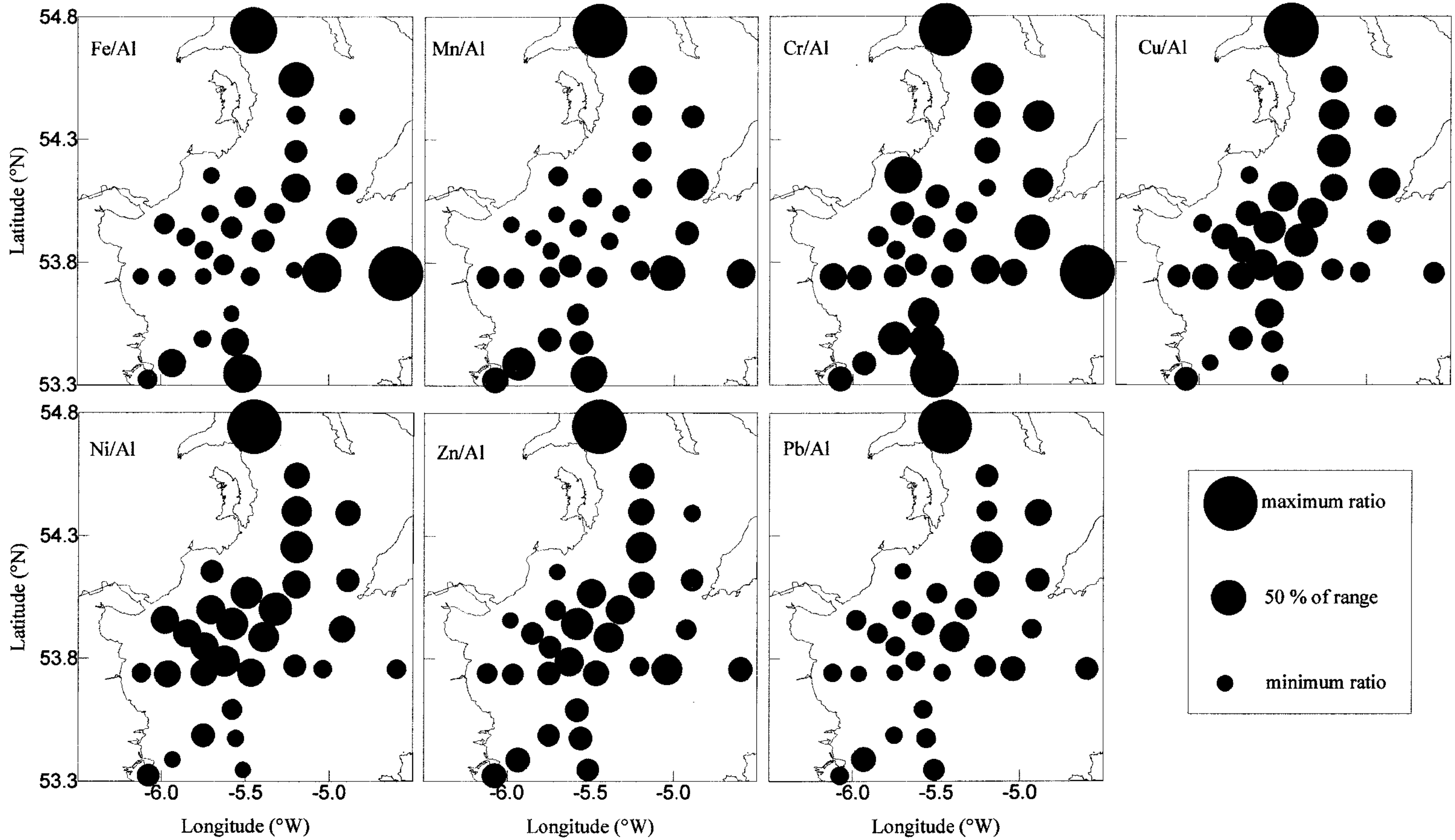

Figure 3. The distribution of metal/Al ratios in the N-W Irish Sea; the size of the circle denotes the value of the ratio

All metals studied showed the highest metal/Al ratios at station 29 in the vicinity of the North Channel disposal ground. Groups of metals with similar biogeochemical behaviour and normalised distributions can be identified. The concentration of Fe, Mn, and Cr showed similar distributions of higher metal/Al ratios to the south-west of the western Irish sea front and north of the study region compared to those in the central seasonally stratified zone. Copper, Ni, and Zn showed greatest ratios (with the exception of station 29) at stations 3 and 5, 8, 11, 12 (which match closely the areas of high stratification found during the spring and summer) and then decreased to the periphery of the north-west Irish Sea. The normalised distribution of Pb also showed high ratios at station 29, however the remaining ratios were comparable to each other with the exception higher concentrations at stations 3 and 12.

During the spring and summer the different water masses within the N-W Irish Sea display different biogeochemical characteristics (Gowen *et. al.,* 1995; Gibson *et. al.,* 1997) that could subsequently cause a difference in the behaviour, transport and hence concentration of metals in sediments. The observed normalised distributions are most likely to be caused by the different biogeochemical response of each metal to the environmental conditions such as redox conditions, and primary production in the overlying water column that would subsequently affect their concentration and thus distributions.

By plotting the concentration of trace metals against Al, antbropogenic contamination can be identified at stations by those lying above the 95 % prediction limits around the regression line (Loring, 1991). Elements strongly affected by redox conditions of the sediment have not been considered as their concentration largely relies on the characteristics of the sediment and to a lesser degree on inputs. Stations that may be considered anthropogenically contaminated by this method are:

Cu : 29, Ni : 29, Zn : 29, Pb : 12 and 3

Station 29 is anthropogenically contaminated with Cu, Ni and Zn which can be attributed to it’s vicinity to the dumping ground in the North Channel. Stations 12 and 3 appear to be contaminated with lead. Williams (1995) suggested that anthropogenic lead is mostly associated with the slowest settling fraction of particulate matter, and so has a potential to be transported far from its source and not settle to the sediment until reaching areas of high water column stability. Hamelin *et. al.,* (1997) demonstrated the ability of oceanographic circulation to advect anthropogenically derived Pb to the subtropical North Atlantic gyre. It would therefore seem possible that anthropogenically derived lead is being transported to this area and allowed to settle to the sea bed in this region of weak currents.

An average of all enrichment factors for the north-west Irish Sea are shown in Table 2, in comparison to those from the North Sea. Background concentrations

Table 2. Metal enrichment factors calculated from data, and from North Sea sediments. a: Irion and Muller (1990); b: Rowlatt and Love11 (1994).

Element	N-W Irish Sea	North Sea[a]	Central North Sea[b]
Pb	2.2	2.8	1.3
Zn	2.1	1.6	1.0
c u	2.0	1.6	n.a.
Cr	1.4	1.2	n.a.

have been taken from a core to the west of the Isle of Man (Pb/Al = 2.3, Zn/Al= 10.1, Cu/Al= 1.6, Cr/Al= 12.6; S. Rowlatt *pers. comm.*)

Factors of metal enrichment in the N-W Irish Sea are higher than values found in the North Sea, which may be indicative of the magnitude of inputs and low currents, allowing particulate bound trace metals to become deposited and retained in the sediments rather than being carried out to the Atlantic Ocean.

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