THE DISTRIBUTION OF TRACE AND MAJOR ELEMENTS IN CHANNEL AND NORTH SEA SUSPENDED MATTER.

1F. DEHAIRS*, 2G. GILLAIN, 1M. DEBONDTE, 1A. VANDENHOUDT
1ANCH, Vrije Universiteit Brussel
B-1050 Brussels, Belgium
2Laboratoire d’Océanologie
Sart-Tilman
Université de Liège
B-4000 Liège, Belgium

ABSTRACT

Size fractionated suspended matter from the English Channel, the Southern Bight and the Central North Sea is analyzed for POC, Al, Fe, Mn, Cu, Zn, Cd and Pb. The Southern Bight area appears to be highly enriched in excess-Fe and -Mn phases, as compared to the Channel and Central North Sea. In the latter area POM is the main component of suspended matter. Pb appears to be associated with aluminosilicates and excess-Fe and -Mn phases. It thus shows higher levels in Southern Bight suspended matter as compared to the central North Sea. Cu and Zn are generally enriched in the fine suspended matter and appear to be correlated with POM. Similarly, Cd correlates with POM, but as opposed to Zn and Cu, it is the coarser plankton that shows the largest enrichment. Increased contents of Cd, but not of Zn and Cu, in plankton with large numbers of the dinoflagellate Ceratium, suggest an active biological uptake for Cd; Cu and Zn are probably scavenged by a fine fraction of detrital POM.

* Research Associate at the National Fund for Scientific Research (Belgium).
1. INTRODUCTION.

The particulate organic matter, the aluminosilicates and the hydroxides and oxides of Fe and Mn represent potential substrates for trace metal scavenging in the marine environment (Duinker, 1981). In the North Sea area the relative contributions of these major components of total suspended matter (TSM) vary considerably with space showing a most drastic change from the shallow (15-30 m) Southern Bight to the deeper (70-100m) central North Sea. In the shallow areas of the Channel and Southern Bight, wind- and tidal current-induced stresses on the sea floor resuspend bottom sediments into the watercolumn. This resuspension determines significantly the composition of TSM. In the Belgian coastal area run-off by the river Scheldt, besides sediment resuspension and epibenthic fluxes is a significant source of aluminosilicates and excess Mn and Fe in suspended matter.

In the deeper central North Sea resuspension of bottom sediments much less affects the composition of the surface water suspended matter. Here the biomass is the major component of TSM.

It is observed that the trace metals considered are affected differentially by uptake or scavenging by the different main particulate phases. As a result regional differences in trace metal content of TSM occur.

2. EXPERIMENTAL.

The data presented here were mainly collected during cruises in the Channel and North Sea in 1983 (figure 1). Some data for the Straits of Dover and the Belgian coastal area were obtained from earlier cruises.
Surface water (-2m) suspended matter was collected underway. The large plankton and seston was fractionized into >215 μm; 215>>100 μm and 100>>50 μm size fractions, by filtration of known large volumes of seawater (up to 3m³) over consecutive plankton nets. Total suspended matter was collected by filtration of small volumes (up to 5 l) over 0.45 μm porosity millipore membranes (Gillain et al., 1984; Gillain and Brihiaye, 1985). Flow through centrifuges were used as well. Centrifuge samples, such as membrane filter samples, are representative of the smaller sized particles composing the bulk of TSM. In Fig. 2, a scheme is shown of the sampling set-up on board the ship.

![Sampling set-up](image)

At station zooplankton was also sampled by net-towing (215 μm mesh size). On board the vessel samples were deep-frozen. In the shore-based laboratory samples were freeze dried and weighed. For the large plankton, if total weight exceeded 200 mg, the sample was grinded and homogenized. Aliquots were taken for POC, PN analysis (Coulometric titration and/or CHN analyser), Chl-a analysis (Strickland-Parsons; Moss-Lorenzen) and metal analysis (Al, Fe, Mn, Zn, Cu, Cd, Pb); HNO₃/HCl mineralisation in PTFE bomb at 80°C then AAS (Flame, GF and ICP). Likewise, membrane samples were dried, weighed and acid mineralized in PTFE bombs for metal analysis. At stations and occasionally underway seawater was filtered on GF/C for POC determination.

The HNO₃/HCl mineralisation in PTFE bombs proved successful for determination of the major metals Al, Fe and Mn. This was tested on a set of sediment samples from the Belgian coastal area and suspended matter samples from the Scheldt estuary. These samples covered a wide range of aluminosilicate content. The samples were analysed for Al, Fe and Mn following a HNO₃/HCl mineralisation described above and a LiBO₂ fusion. Both methods gave similar results for Al, Fe and Mn.

For discussion of the metal data below we have considered the ex-
cess-amounts of each element (excepted organic C and Al). These excess-amounts are the total concentration minus the concentration supported by inorganic, detritic components (see f.i. Sholkovitz and Copland, 1982). The composition of average soil, given in Bowen (1979), is considered to represent the reference situation with no metal excess. Excess-metal contents are thus calculated as:

\[(X)_{\text{excess}} = (X)_{\text{total}} - (X/Al)_{\text{soil}} \times (Al)_{\text{sample}}\]

3. RESULTS AND DISCUSSION.

In table 1 we have compiled the POC and excess-metal data for the three main geographical areas studied: the Channel, the Southern Bight and the central North Sea.

TPM. It appears that the membrane samples represent some 90% of TPM. For the plankton > 50 \(\mu m\) there is a trend for decreasing TPM concentration with increasing particle size. However, the samples from the central North Sea behave differently in that here the 215 >> 100 \(\mu m\) size class has a high TPM concentration relative to the 100 >> 50 and the > 215 \(\mu m\) size classes. For this area large amounts of the dinoflagellate Ceratium were observed by microscopic inspection of separate plankton samples (M.H.Daro, pers.comm.). Therefore, Ceratium is most probably responsible here for the high TPM content in the 215 >> 100 \(\mu m\) size fraction.

POC. Highest POC contents are observed in the > 215 \(\mu m\) fractions, mainly composed of zooplankton. POC contents of the fractions < 215 \(\mu m\) increase strongly in the central North Sea as compared to the Southern Bight and the Channel. A decrease of detritic inorganic components (quartz, aluminosilicates) in the watercolumn of the central North Sea is the main reason for these increased POM contributions to TPM.

Al, Fe and Mn. For all size fractions, relative Al contents decrease sharply from the Southern Bight to the central North Sea due to a decreased impact of sediment resuspension on surface water suspended matter composition (table 1). The highest contents of excess Fe and Mn, for all size fractions, are observed in the Southern Bight. Excess Mn and Fe decrease in the central North Sea, but not as strongly as Al, thus giving rise to the highest Mn/Al and Fe/Al ratios observed in this study. Excess Mn is lowest in the Channel area.

From figure 3, in which total Mn over Al is plotted against total Fe over Al, it is clear that most of the North Sea area investigated is characterized by the presence of excess-Mn and -Fe. Only a few samples from the Channel, the Dover Straits and the Southern Bight show no enrichment. The geographical variability discussed above is better represented by plotting the Fe/Mn ratios against the Mn/Al ratios (figure 4).
<table>
<thead>
<tr>
<th></th>
<th>CHANNEL I</th>
<th></th>
<th>SOUTHERN BIGHT II</th>
<th></th>
<th>CENTRAL NORTH SEA III</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt;0.45</td>
<td>50&lt;100</td>
<td>100&lt;215</td>
<td>&gt;215</td>
<td>&gt;0.45</td>
<td>50&lt;100</td>
</tr>
<tr>
<td>TPM mg/l</td>
<td>3.8</td>
<td>0.16</td>
<td>0.12</td>
<td>0.13</td>
<td>7.1</td>
<td>0.23</td>
</tr>
<tr>
<td>%</td>
<td>100</td>
<td>4.2</td>
<td>3.2</td>
<td>3.6</td>
<td>100</td>
<td>3.3</td>
</tr>
<tr>
<td>POC mg/g</td>
<td>130</td>
<td>51</td>
<td>71</td>
<td>224</td>
<td>66</td>
<td>61</td>
</tr>
<tr>
<td>Al tot. *</td>
<td>7,026</td>
<td>17,084</td>
<td>14,534</td>
<td>5,525</td>
<td>11,988</td>
<td>11,000</td>
</tr>
<tr>
<td>Fe exc. *</td>
<td>2,994</td>
<td>719</td>
<td>454</td>
<td>500</td>
<td>7,683</td>
<td>5,220</td>
</tr>
<tr>
<td>Mn exc. *</td>
<td>28</td>
<td>0</td>
<td>4</td>
<td>5</td>
<td>228</td>
<td>69</td>
</tr>
<tr>
<td>Zn exc. *</td>
<td>433</td>
<td>50</td>
<td>57</td>
<td>108</td>
<td>305</td>
<td>87</td>
</tr>
<tr>
<td>Cu exc. *</td>
<td>23</td>
<td>8</td>
<td>10</td>
<td>11</td>
<td>18</td>
<td>8</td>
</tr>
<tr>
<td>Pb exc. *</td>
<td>39</td>
<td>55</td>
<td>54</td>
<td>52</td>
<td>71</td>
<td>41</td>
</tr>
<tr>
<td>Cd exc. *</td>
<td>1.3</td>
<td>3.4</td>
<td>4.8</td>
<td>2.3</td>
<td>1.1</td>
<td>3.6</td>
</tr>
<tr>
<td>(N)</td>
<td>(14)</td>
<td>(7)</td>
<td>(9)</td>
<td>(4)</td>
<td>(10)</td>
<td>(8)</td>
</tr>
</tbody>
</table>

(N) = number of samples; size fractions in μm; * concentrations in μg/g.
From figure 4 it appears that going from the Channel, through the Belgian coastal area and the Southern Bight to the central North Sea, Mn enrichment increasingly exceeds the Fe enrichment.

As concerns the shallow Southern Bight area this excess-Mn and -Fe can be introduced in the watercolumn by: (1) resuspension of bottom sediments carrying excess-Mn and -Fe; (2) outflux of dissolved, reduced Mn and Fe species from the sediments; (3) outflux of suspended matter enriched in Mn and Fe from the Scheldt.

Inspection of Fe/Al and Mn/Al profiles in cores from the offshore sandy area (Cores Pt33; Pt34) and the inshore (Zeebrugge; M1149) mud area in the Belgian coastal zone (figure 5), shows that resuspension of bottom sediments can introduce excess metals in the sandy area, while for the mud area outflux of
reduced Mn and Fe followed by precipitation of their oxides and hydroxides in the watercolumn is possible. Output of Mn by the Scheldt river (400 Ton. Y\(^{-1}\));

Figures 5: Belgian Coast; total Fe/Al and total Mn/Al ratios in cores from a sandy area (Pt 33, Pt 34) and in a core from a mud area (M1149). Only for the latter core, diss. Fe and Mn were present in detectable amounts.

Wollast, 1976; Duinker et al., 1979) exceeds the residual-flow throughput in the Belgian coastal area, calculated as 250 Ton. Y\(^{-1}\) (conditions: Water inflow \(\approx 500\) km\(^3\). Y\(^{-1}\) (Baeyens et al., this volume); conc. of part. Mn at western boundary: 0.48 \(\mu\) g. l\(^{-1}\), this study), stressing the importance of river run-off as a source of excess-Mn in the area.

Figures 6: South-north profiles in the North Sea of excess-Cd, excess-Pb, excess-Zn and excess-Cu for the > 0.45 \(\mu\) m size fraction.

Lead. From table 1 it appears that the fine suspended matter (i.e. the > 0.45 \(\mu\) m fraction) in the Southern Bight has the highest Pb contents. The longitu-
dinal profile, through Southern Bight and central North Sea for the > 0.45 μm fraction shows a decrease in excess Pb content from south to north (figures 6). This decrease parallels those of Fe, Mn and Al (table 1). Thus, excess Pb is positively correlated with excess Fe and Al, (figures 7) but also excess Mn (not shown here). Therefore, it appears likely that Pb is associated mainly with inorganic phases, both of detritic and authigenic origin.

Figures 7: Excess-Pb versus excess Fe and total Al, for the > 0.45 μm size fraction in the Channel and the North Sea (A,C); excess Pb versus excess Fe for the 215 >> 50 μm size fraction in the Central North Sea (B).

Pb scavenging by redox-processes at the sediment-water column boundary was invoked by Spencer et al. (1980) in order to explain observed 210Pb profiles in the North Sea.

Cu and Zn. The fine particulate matter (i.e. the > 0.45 μm fraction) in the Channel, Southern Bight and central North Sea shows highest contents of Zn and Cu as compared to the larger size fractions. If we consider all size fractions < 215 μm a gross positive correlation with POC is apparent (table 1), with a general increase of POC and Zn contents from the south to north (figures 6). In figures 8, the Zn and Cu data are plotted against POC for the 100 >> 50 and 215 >> 100 μm size fractions. The same approach was not possible for the > 0.45 μm fraction, since for this size fraction metals and POC were not measured on the same samples. From figures 8 the positive correlation is clear for Zn-POC but much less so for Cu-POC. This figure also shows that the correlations disappear for samples taken north of 57°N, where Ceratium is a major constituent of the 215 >> 50 μm plankton. This latter fact, together with the observation that the fine particulate matter generally contains the
highest Zn and Cu contents, suggests that Zn and Cu are mainly associated with small sized detrital POM.

Figures 8: Excess Zn and excess Cu, versus POC for the 215 >> 50 size fraction in Channel, Southern Bight (I + II) and Central North Sea (III).

Cadmium. The large-sized suspended matter and plankton ( > 50 µm) has higher excess Cd levels than the fine suspended matter (table 1). For all size fractions a two-fold increase in Cd content is apparent between Southern Bight and central North Sea. Such as for Zn and Cu, Cd in the fine suspended matter increases from south to north (figures 6). But, unlike Zn and Cu, Cd in the larger plankton (50 << 215 µm) correlates with POC even for the area north of 57°N where the Ceratium-enriched plankton occurs. Thus a correlation with POC is apparent, but the generally increased Cd contents in the larger plankton and the increased contents when Ceratium is present suggest an uptake of Cd by living plankton. This corroborates findings by other researchers (e.g. Boyle and Huested, 1983; Bruland and Franks, 1983) showing a close similarity in the oceans between the behaviour of the limiting nutrient P04 and Cd.

4. CONCLUSIONS.

The suspended matter in the Southern Bight area is characterized by a larger contribution of excess Mn, excess Fe and aluminosilicates as compared to the Channel and the central North Sea. These phases appear to control the Pb distribution in the area, probably through scavenging processes. As a result particulate Pb contents of the suspended matter are higher in the Southern Bight area.

Zn and Cu contents, on the contrary, increase northwards with increasing POC contents. Evidence is found that Zn and Cu are associated rather with detrital POM and are not actively taken up by the plankton. Cd behaviour is similar to
the one of Zn and Cu in that a correlation with POM is apparant. However, increased Cd contents in suspended matter containing well-identified living plankton (Ceratium) suggests an active uptake by the plankton.

ACKNOWLEDGEMENTS

We thank the Belgian Ministry of Science Policy (grant n°83/88-56) and the European Communities (grants ENV-566-B, ENV-766-B) for financial support of this research. The Management Unit North Sea and Scheldt Estuary is thanked for its logistical assistance during the cruises.

REFERENCES

Baeyens W., Gillain G., Djenidi S., Hoenig M., Wartel S., Dehairs F.; Metal flows in, out and through the Belgian coastal waters, see this volume.

***