Copper, lead and zinc in salt marsh sediments of the Severn Estuary, UK: the potential for their early diagenetic mobility

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Abstract

A detailed lithostratigraphic analysis already exists for salt marsh sediments of the Severn Estuary, which provides an ideal background for an investigation of phase associations of trace elements within sediment depth profiles. The first stages of a detailed investigation are reported in which phase associations of Cu, Pb and Zn are related to early diagenetic processes.

Introduction

Estuaries are commonly sites for the disposal of a wide variety of waste products including trace metals which are often assumed to associate with sediments, and therefore to have the potential for "removal" from the system when the sediments are deposited. It may be, however, that in addition to the possibility of physical resuspension of sediments (Luther et al., 1986), significant early diagenetic remobilisation of pollutants may take place (Elderfield and Hepworth, 1975). An understanding of the nature and extent of this remobilisation is a crucial part of environmental quality assessment.

The Severn Estuary on the south-west coast of Britain is a large, macrotidal and well mixed system, receiving pollutant metals from a wide variety of sources. Owens (1984) has detailed the significance of different sources and amounts of recent contaminant inputs to the estuary and data for Cu, Pb and Zn are presented in Table 1. It is interesting to note that the major source of Cu to the estuary is from rivers and streams whereas the atmospheric input is dominant for Pb and Zn.

The scenery of the shore-line in the intertidal zone of the estuary is very striking, with bold mud cliffs up to 10 m in height cutting back into salt marsh sediments. These cliffs are actually complex features resulting from the oscillating retreat and advance of the shore-line under the influence of a variety of natural forces (Allen, 1989). Allen and Rae (1987) carried out a reconnaissance study of the mud cliffs and recognised at least four discrete lithostratigraphic units (Figure 1). It was considered that this mud cliff stratigraphy provided an important background from which a study of the trace element geochemistry of sediments from the cliffs may be usefully carried out. Such a study would provide information on any early diagenetic mobility of trace elements and may also allow some understanding of possible changes in sources and amounts of contaminants with time. The work presented in this paper is an investigation of the phase associations of Cu, Pb and Zn in a small number of sediments from marsh cliff depth profiles. It represents the initial phase of an extended study.

Methods

Samples were collected from trimmed mud cliff sections at Peterstone Wentlooge (Wentlooge and Rumney formations) and from Woolaston (Awre and Rumney formations), Figure 2. Thin walled plastic tubes (100 x 43 mm) were pushed horizontally into the cliffs at fixed intervals of 0.05/0.1 m. In the laboratory, samples were extruded from the tubes and air dried. They were coarsely crushed and split by coning and quartering. Approximately one quarter of each sample was retained and the remainder was ground for Pb and Zn.

The clay fraction of the unground sediments was separated by sedimentation and analysed by X-ray diffraction using...
Results and Discussion

Results of the X-ray diffraction analysis are presented in Table 2. The detrital minerals which are present throughout the section are quartz, plagioclase and alkali feldspar, mica, chlorite and kaolinite. Haematite is probably also detrital, since it is known to exist as a fine grained surface coating on much of the source sediment. Unlike the other detrital minerals, however, haematite was not detected in the oldest (Wentlooge formation) sediments. This suggests that reducing conditions may exist in the sediments of the Wentlooge formation which could cause the redistribution of haematite and possibly any other Fe/Mn oxides/hydroxides, together with any co-precipitated Cu, Pb and Zn. Calcite may be detrital, but may also form during early diagenesis (Curtis, 1977). It is likely that the siderite is all diagenetic (Garrels and Christ, 1965). Aragonite may also exist in the sediments as shell material, but its identification by X-ray diffraction is difficult due to ion oxide peak overlap.

Percentages of organic carbon and carbonate carbon are given in Table 3. Carbonate carbon varies from 0.009% to 1.35%, the higher values possibly relating in part, to the existence of shell material at particular horizons in the section. Organic carbon percentages show an overall decrease with increasing depth and increasing age, relating to the breakdown of organic matter during diagenesis. The three highest values of organic carbon relate to the three horizons in which coal and organic matter was obvious by visual inspection.

Tables 4-6 contain the results of the phase association extractions for Cu, Pb and Zn, and a comparison of extraction totals (obtained by summing the amounts of elements in each phase, for each sample), with the values obtained from the X-ray fluorescence analysis. There is very good agreement between the two techniques for the majority of these totals. The values for the three sediment samples at the base of the section may be considered to represent unpolluted sediments whereas those lying above have been subject to anthropogenic pollution (Allen and Rae, 1987).

Table 1 Contributions (%) from rivers, sewage, industrial effluent, atmospheric deposition and sludge to total Cu, Pb and Zn input to the Severn Estuary. (After Owens, 1984).

<table>
<thead>
<tr>
<th>Element</th>
<th>Rivers and streams</th>
<th>Domestic sewage</th>
<th>Industrial effluent</th>
<th>Atmospheric input</th>
<th>Sludge dumping</th>
</tr>
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<tbody>
<tr>
<td>Cu</td>
<td>54.2</td>
<td>8.6</td>
<td>15.8</td>
<td>19.0</td>
<td>2.4</td>
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<tr>
<td>Pb</td>
<td>16.9</td>
<td>4.5</td>
<td>18.5</td>
<td>57.8</td>
<td>1.9</td>
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<tr>
<td>Zn</td>
<td>30.3</td>
<td>8.8</td>
<td>17.8</td>
<td>42.2</td>
<td>0.9</td>
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</tbody>
</table>