

The use of sediments in pollution studies

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Sediments reflect the general quality of the marine environment. Scientists in the ICES community have, for many years, been attempting to gain international agreement on how sediments can be used to show spatial or temporal variations. There have been many debates about how to use sediments, but only in the last year has an element of agreement been achieved. This paper describes the objectives of such monitoring and how agreement has been reached.

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Introduction: sediments as a medium for assessing environmental quality

Sediments are widely recognized as a suitable medium for assessing environmental quality as they reflect and integrate contaminant inputs to the marine environment and allow sources and sinks to be identified (e.g., ICES, 1989). Also, the monitoring of contaminants in sediment is becoming increasingly recognized as important because sediments can act as a reservoir or long-term sink for many metals and hydrophobic organic contaminants. A third factor favouring the use of sediments for monitoring environmental quality, particularly for organic compounds, is that concentrations are relatively high compared with those in seawater, thus making analysis more straightforward.

Unfortunately, while most workers agree on the value of sediments as a tool for environmental monitoring, until very recently, there has been no widespread agreement on how to use them (i.e., the sampling and analytical procedures).

The ICES Working Group on Marine Sediments in Relation to Pollution has, amongst other things, spent much time over the last 20 years trying to decide on advice about sediment monitoring and how to use sediments to assess man's influence on the environment.

The problem: agreeing a method

While sediments are accepted as a suitable medium for environmental monitoring, the method of carrying out such monitoring has been difficult to agree. One of the

greatest difficulties is to decide how anthropogenic effects can be detected. In recent years, ICES has been associated with attempts to coordinate sediment monitoring throughout Europe. Such coordination should ensure that all collaborators collect sediments in the same way, process the sediments in the same way, analyse the sediments in the same way, and interpret the resulting data in the same way. If the data were coordinated, comparison between areas would be relatively straightforward and would not suffer the confusion or uncertainty as at present.

The solution?: normalization

One important component in the area of intercomparability is how to interpret data from sands and mud. The technique of normalization has found favour in attempts to compare sediments of different types (e.g., sand and mud).

In general, metal concentrations in sediments are higher in areas of fine-grained sediment. It is important to separate the various factors leading to these relatively high concentrations before conclusions are drawn concerning the degree of contamination. Clay minerals, a major component of much fine-grained sediment, have a relatively high natural metal content compared with sand and also a greater active surface area, which may sorb metals. This causes sediment metal concentrations to be generally higher in areas of mud than in sandy regions. The effect is demonstrated in coastal areas where the muddier estuarine samples can be seen to contain higher concentrations of aluminium, a significant component of clay minerals. Such mineralogical

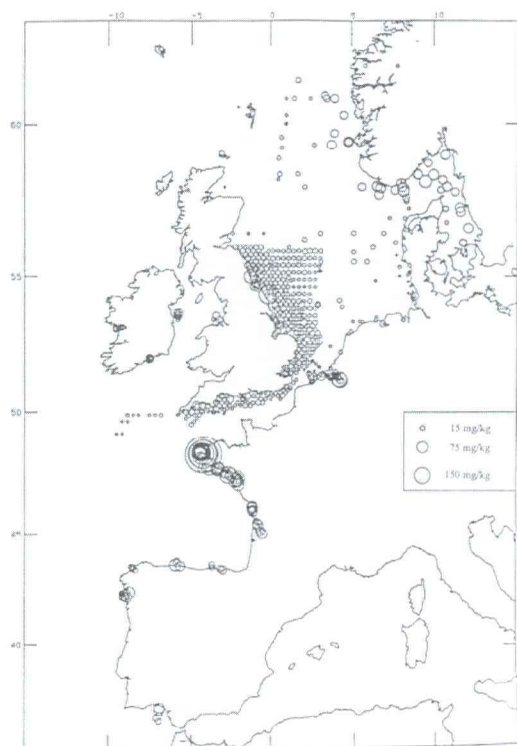


Figure 1. Spatial distribution of lead in sediments in Europe (SEDMON).

and grain-size effects can confound attempts to compare metal concentrations throughout a given area, but may be taken into account by using a normalization procedure (ICES, 1989; Loring, 1991).

In the present context, normalization requires the use of a non-contaminant element associated with clay minerals to account for mineralogical variations. Two potential normalising elements are aluminium and lithium. Both of these elements are present in clay minerals, and each may act as a surrogate for the clay mineral fraction.

Several methods of normalization are possible, ranging from the use of simple metal/normalizer ratios to more complex methods based on regression analysis. As some of the metal/normalizer regressions often have significant intercepts on the metal axis, the simple metal/aluminium ratio can lead to spuriously high values at low normalizer concentrations. Therefore, it is often better to use a method less sensitive to the effects of an intercept value. The technique used in the SEDMON (ICES/NSTF/OSPARCOM *ad hoc* Working Group on Sediment Baseline Study Data Assessment) exercise (Rowlatt and Davies, 1995) is based on a metal/normalizer regression model with calculation of residuals about the regression line.

Various authors have favoured different normalizers. For example, Schropp and Windom (1988), working in Florida, preferred aluminium, while Middleton and

Grant (1990), in the Humber, used rubidium. Loring (1991) recommended the use of lithium in areas with sediments derived by glacial processes where aluminium may be present in feldspars in the sand-sized sediment fraction. North Sea sediments, when aluminium is normalised against lithium, indicate an excess of aluminium in the northern North Sea (Rowlatt and Lovell, 1994). This suggests that the effect described by Loring does, to a degree, affect North Sea sediments. However, an examination of sediment metal concentrations in the North Sea (Rowlatt and Lovell, 1994) has shown little difference in the final results obtained using lithium and aluminium as normalizers, indicating that any such effect is only minor. As, first, there was little difference in the overall distribution patterns produced using these two normalizers and secondly, aluminium is more widely accepted as a normalizer, Rowlatt and Lovell (1994) preferred aluminium to lithium as a normalizer. This was a pragmatic solution, which may be most suitable for North Sea sediments, although its limitations in glacial areas must be borne in mind (Loring, 1991).

Using the agreed method for spatial analysis: SEDMON

In the late 1980s, the Joint Monitoring Group (JMG) of the Oslo and Paris Commissions initiated an international programme to assess the spatial distribution of metals and organic substances in marine sediments throughout the Joint Monitoring Programme (JMP) area. Twelve countries collected seabed samples for this "JMG Baseline Sediment Study" in 1990 and 1991 (see Figure 1). Data from analyses of the samples were submitted to ICES and combined with results produced for the North Sea Task Force (NSTF) assessment of the quality of the North Sea. The North Sea component of the dataset (data from eight countries) was assessed by SEDMON in May 1992 for use by the NSTF in the 1993 QSR. In December 1992, the whole dataset was assessed by the *ad hoc* Working Group of the JMG (ADHOCMON92).

One of the main tasks of the North Sea Task Force was the preparation of the North Sea Quality Status Report (QSR), which was published in 1993 (North Sea Task Force, 1993). At their joint meeting in June 1991, the Oslo and Paris Commissions (OSPARCOM) agreed that monitoring data to be fed into the preparation of the QSR would be considered in two different data sets:

- 1) the "historical data", mainly from 1985 to 1989, and
- 2) the NSTF Monitoring Master Plan (MMP) data and other relevant data for the years 1990 and 1991.

OSPARCOM further agreed that the data to be considered on contaminants in marine sediments for 1990–1991 should include MMP data and also data from the

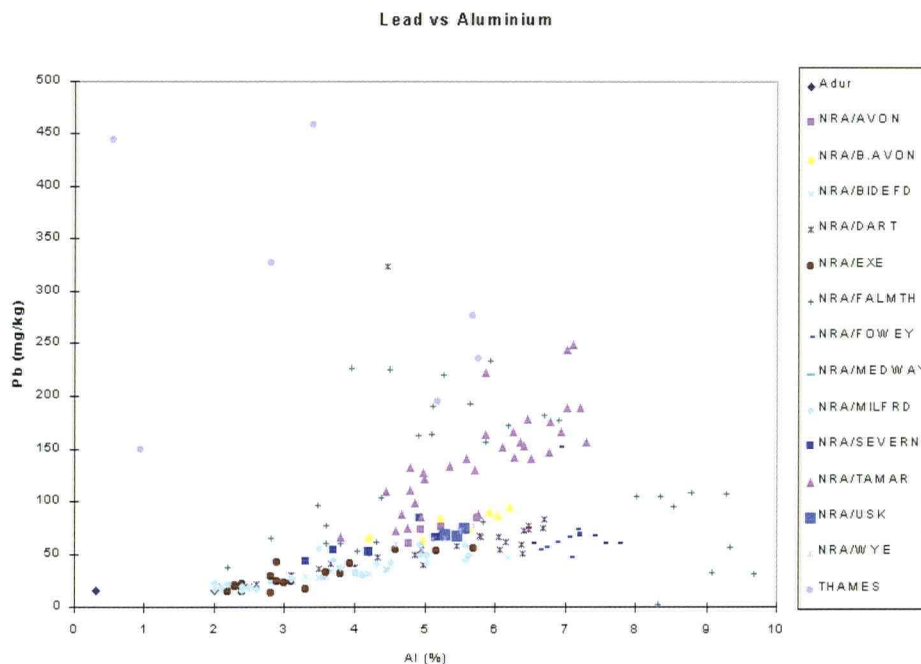


Figure 2. Lead and aluminium in various estuarine sediments.

JMP of OSPARCOM. In order to meet the deadline of July 1992 for submissions to be incorporated into the QSR, pre-assessments of the unvalidated data were carried out by national experts in April 1992. A joint ICES/NSTF/OSPARCOM *ad hoc* Working Group on Sediment Baseline Study Data Assessment (Rowlatt and Davies, 1995) was convened in Copenhagen, 27 April–2 May 1992, in order to assess the data and prepare data products. Rowlatt and Davies (1995) summarized the findings of that group. In that assessment exercise, only data from the NSTF area were taken into account, which included the North Sea proper, the northern North Sea, the Kattegat and Skagerrak, and the English Channel.

The data on contaminants in sediments reviewed here represent a subset of the data collected for the OSPARCOM area as a whole (i.e., the Northeast Atlantic); the full data set was assessed at the end of 1992.

The aims of the SEDMON assessment were as follows:

- a) to describe the variations in metal and organic contaminant concentrations (whether normalized or not) in the North Sea;
- b) to describe the metal and organic contaminant concentrations at the MMP sites;
- c) to relate variations in concentration (whether normalized or not) to known inputs; and
- d) to make recommendations for future work.

SEDMON found higher concentrations of metals in areas close to industrial sources (e.g., the Norwegian

fjords, the Elbe, Scheldt, Seine, Humber, Tyne, and Tees rivers) and in areas near zones of mineralized rocks (Norway, Helgoland, southwest England, and northwest England). Unfortunately, only a limited amount of data was submitted concerning organic contaminants, and conclusions were hard to draw.

However, the SEDMON method has been found useful in the interpretation of other sediments (Figure 2).

A method for temporal trend measurement

Each year about 1.5 million wet tonnes of sewage sludge were deposited at a designated site in Liverpool Bay by North West Water Limited. The Burnham Laboratory of the UK Centre for Environment, Fisheries and Aquaculture Science has studied the area since the 1970s to determine any effects on water, sediment, or fish quality. This work has included the analysis of sediment samples collected near the disposal site where effects on sediment chemistry have been observed (Norton *et al.*, 1984, and unpublished data).

Sediment samples were collected using a 0.1 m² Day Grab. Samples of the upper 0–1 cm of the sediment were stored frozen for later chemical and physical analysis. On return to the laboratory, the sediments were defrosted and sieved to extract the fine fraction (<90 µm).

The fines were subdivided and the carbon content of one subsample determined instrumentally, after pre-

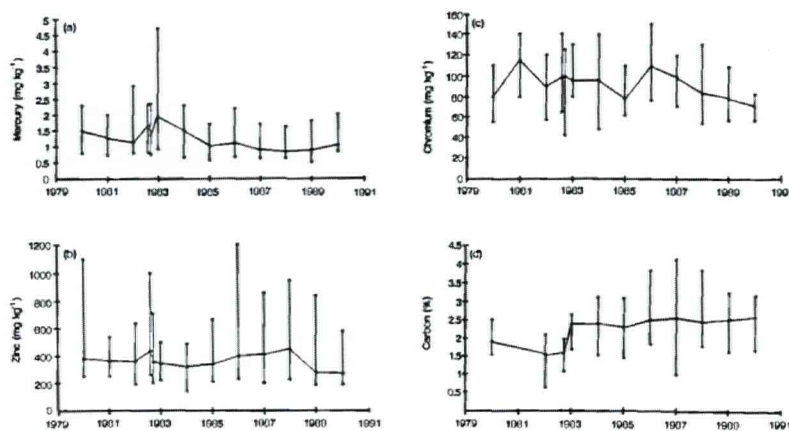


Figure 3. Temporal trends in Liverpool Bay sediments.

treatment with sulphurous acid to remove any carbonates present. Another subsample was digested with aqua regia and the metals mercury, copper, chromium, nickel, lead, and zinc determined by atomic absorption spectrophotometry.

Concentrations of trace metals in the sediments exhibit highly non-normal distributions and are, therefore, described using non-parametric measures. Figure 3a–c shows the median and range of concentrations of mercury, zinc, and chromium from 1980 to 1990. The most notable feature of the time-series is the absence of any marked trend over the decade of study. Figure 3d shows carbon data presented in the same manner as the metal data. This shows a consistent median value during the period 1983–1990, although it appears the concentrations may have been slightly lower in the early years of the decade.

The concentration ranges show considerable overlap between all years. This suggests that when considering data from this sandy area, it should be recognized first that the $<90\text{-}\mu\text{m}$ fraction, in general, represents less than 5% of the total sediment and secondly that, when considered on a whole sediment basis, the concentrations of metals are very low. It is known that sediments in the vicinity of the disposal site contain higher concentrations of several metals (e.g., copper, mercury, zinc, and lead) than sediments further away (Norton *et al.*, 1984). It seems reasonable to conclude that there has been some accumulation of metal contaminants in the area as a direct consequence of the sewage-sludge disposal operation. However, the fact that there has been no increase during the last 10 years indicates that the sys-

tem is in a steady state and has been so for at least the last decade.

Continuing differences, recent WGMS agreement

The ICES Working Group on Marine Sediments in Relation to Pollution (WGMS), after much disagreement, produced, in 2000, advice on the use of sediments for spatial monitoring. This took account of the SEDMON and OSPAR experience as well as the national advice from various studies around the world.

The WGMS advice on which method to use is only provisional, as it has not yet been approved by the ICES Advisory Committee on the Marine Environment. The advice recommends the use of analyses of a fine fraction of sediment ($<63\text{ }\mu\text{m}$) as the preferred fraction to measure. It also recommends the use of a strong acid digestion procedure and the use of reference material.

Thus, the Working Group has come to the end of a long period of serious disagreement by deciding which size fraction of sediments to use and which method to use when analysing them. The Group has reached agreement in which nearly everyone has had to compromise, for the good of all. It is worth noting that, over a period of 10 years, there have been many arguments and disagreements, but that the strength of ICES has shone through, and everyone has continued to work for the common good.

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