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Spatial clustering of metals in the sediments of the Skagerrak/Kattegat

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Abstract

The present work attempts to describe the spatial distribution of heavy metals in the surficial sediments of the Kattegat and Skagerrak. It is based on multivariate statistical analyses. Principal Component Analysis is used to gain information on the chemical characteristics of the metals as a group. Cluster analysis is used to classify the sampling stations into groups regarding the principal components. In addition, cluster analysis is adopted directly on the metals. Together these enable an interpretation of the processes involved in the formation of these coastal sediments. It is seen that the main factors controlling the composition of the clusters are the chemical characteristics of the data and not the sources. A few exceptions are found though, where direct point sources are identified.

1. Introduction

Heavy metal contamination is not a modern problem arising from industrialisation; it began when humans started processing ores (Renberg et al., 1993). Since then the use of metals and their impact on the environment has accelerated, with a major increase during the 19th and 20th century (see review in e.g., Förstner and Wittman, 1983). During the last decades the heavy metal load, introduced by man, has been equal to or larger than the natural one (Bruland et al., 1974). A large proportion of the heavy metals dispersed to the air and/or directly into rivers, ends up in coastal sediments (see reviews in e.g., Cato, 1977; Förstner, 1980; Salomons et al., 1988). Consequently this zone is an effective sink for most metals—naturally as well as anthropogenically introduced to the sea (e.g., Salomons and Förstner, 1984; Holligan and de Boois, 1993; Cato, 1997a). However, sediments may also act as metal sources, especially in the coastal zone.

The awareness of sediment incorporation of heavy metals of anthropogenic or natural origin has led to concern about the quality of the marine environment but also an increased use of sediments as a tool in assessing the impact of anthropogenic emissions on the environment.

The main objective of this study is to investigate metal interrelations, classify groups of samples in the surficial sediments of Kattegat and Skagerrak and to decide factors that affect their spatial distribution. A comparison with the metal concentrations in a subsur-

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face layer was also made to see if there has been any change over time. Multivariate statistical methods were used throughout the work.

2. Methodology

Principal Component Analysis (PCA) was used to characterise the metal composition in the sediments while cluster analysis was used for grouping the stations.

2.1. Principal Component Analysis

PCA is a multivariate method mainly used for data reduction. It aims at finding a few components that explain the major variation within the data. Each component is a weighted, linear combination of the original variables. Usually only components with eigenvalue >1 are of interest. In order to make the components more interpretable, while still being orthogonal, a varimax rotation is used.

As PCA analyses several variables simultaneously it is suitable for analysing sediments, where each sample contains the concentrations of several variables. It has already been used in a number of metal applications, where the general metal composition in the environment is studied (e.g., Ebsen et al., 1987; Lindqvist et al., 1987; Hallberg, 1991; Armanino et al., 1996; Davies, 1997).

2.2. Clustering

Clustering is a popular technique used in many different disciplines, e.g., biometrics (Mantel, 1967; Patterson and Waugh, 1992), biochemistry (Reyment, 1996), biogeochemistry (Karydis, 1992) and biology (Clarke and Green, 1988). It is a series of multivariate methods that is used to find 'true' groups of data, here groups of stations. Perhaps one of the most interesting features is when unexpected groups are found, as these reveal some unknown information about the data. In clustering the objects are grouped so that 'similar' objects fall into the same class. Objects in one cluster should be homogeneous, with respect to some characteristics describing the within cluster properties, and well separated from the elements in other clusters. This separation of clusters is based on some multivariate distance. Usually this is some variation of the Euclidean distance, based on variable values (here concentrations), but it may also be based on correlation or covariance.

Clustering techniques can be divided into two major groups—hierarchic and non-hierarchic methods. In the former, which is used in this study, the data are strictly given cluster identification, an identification that cannot be changed. This means that the cluster procedure can only act on the clusters fused at earlier steps and not reconsider what was created previously. On the other hand, it has the advantage of not demanding any a priori knowledge of the number of clusters, which the non-hierarchic grouping does. As no information exists about the true number of clusters, a dendrogram is usually used to choose the number of clusters (see Sharma, 1996, for a description).

There is always a question of which clustering procedure is the most suitable. In a review by Sharma (1996), Ward's minimum variance technique was superior, in the sense of giving a larger amount of correct classified observations, to most other methods. Also average linkage clustering was found to give better results than most other methods tested. Massart and Kaufman (1983) support this conclusion. Consequently, these two methods have been chosen for this study. As a distance measure the squared Euclidean distance was used, which is one of the most commonly adopted measures (Fovell and Fovell, 1993).

If the original variables are highly correlated the information being clustered is redundant making the orthogonal principal components favourable in clustering (Fovell and Fovell, 1993). However, as the first components (eigenvalue >1) only cover the major part of the variation some infomation in the remaining part is left out. Additional information may be obtained through clustering of the original variables as well.

2.3. Average linkage clustering

Average linkage is one of the most frequently used clustering methods. The agglomeration starts with n clusters (each containing one station). In each step, the average Euclidean distance between all pairs of objects from each of two clusters is calculated. The cluster pair with minimum separation distance will form a new cluster. This will continue until one all-inclusive cluster is created. The distance measurement is unweighted. Therefore, the 'midpoint' between two clusters will not be found in the centre, but closer to the larger of the two.

2.4. Ward's minimum variance clustering

Ward's clustering uses an intracluster variation instead of the Euclidean distance. It forms clusters by maximising the homogeneity within each cluster, which is equal to reducing the total within-cluster variation. This variation is defined as the sum of squares of the distances between every point in the cluster and the cluster centroid. In each step, the two clusters with the lowest intracluster variation will be joined.

A disadvantage with Ward's method is that it tends

to join small clusters and is biased towards producing large, equally sized clusters. When using Ward's minimum variance clustering with equal weights, i.e., equal weight to each element in the cluster, these weights will be proportional to the size of the cluster. Therefore the new 'centre' will not be located exactly between the two previous clusters, but closer to the larger of the two. There are alternatives with weighted average distances, but they are not used in this study. This decision is supported by e.g., Pielou (1984), who has shown that unweighted clustering is normally the best choice.

3. Areas of investigation

The study area and the spatial location of the stations are shown in Fig. 1.

3.1. Hydrography

Kattegat has an area of 17 700 km^2 and a volume of 375 km^3, with an average depth of 20 m. A halocline is present throughout the year (at an average depth of 15 m). Mixing across the halocline is dominated by wind-driven upward entrainment. For surface water the average residence time is 2 months. Corresponding time for the deep waters is up to 4 months (Andersson and Rydberg, 1988). Deep-water inflow is calculated to be 64 000 m^3 s^{-1} during winter and slightly less, 50 000 m^3 s^{-1}, during summer (Andersson and Rydberg, 1993).

The Skagerrak has a surface area of 32 000 km^2 and an average depth of 200 m. Maximum depth (~700 m) is found in the Norwegian trench (see Fig. 1). A strong anticlockwise circulation, which reaches down to bottoms at 400–500 m, dominates the water movement (Rodhe, 1996). The average residence time for water is 3–4 months (Rosenberg et al., 1996).

Since the study area is situated between the brackish Baltic Sea and the marine North Sea, the salinity shows a NW–SE gradient. There is also a minor gradient in longitudinal direction, due to freshwater inflow. Lowest salinity can be found close to the Swedish coast in the Katteget (Andersson and Rydberg, 1993). For surface water the salinity is 15–30 PSU (practical salinity units) and in the deep water 32–34 PSU.

3.2. Sedimentological settings

Sand and coarse silt, mainly underlain by glacial clay, dominate the shallow area of the Kattegat and northwestern Skagerrak off Jutland. Areas with water depths of more than 75 m are dominated by Holocene clayey sediments, with an organic content of about 2–3% dry matter. These sediments also dominate the sheltered parts of the archipelago and in the fjords of the Skagerrak (Cato, 1992; Kuijpers et al., 1992; Geological Survey of Sweden, 1989, 1994, 1997). Skagerrak's fine grained sediments are deposited with an annual rate of approximately 2 mm at the slopes, 1 mm in the deepest parts and more than 4 mm in the northeastern part of the Norwegian trench (van Weering et al., 1987; Kuijpers et al., 1993; Bøe et al., 1996; Kunzendorf et al., 1996). In the deep areas of the northwestern Kattegat extreme sedimentation rates of roughly 100 mm a^{-1} have been reported (Rodhe, 1973). Cato (1997b) reports sedimentation rates between 1.3 and 14 mm a^{-1} from the coastal zone along the eastern Skagerrak coast.

In total around 30 million tonnes (dry weight) are deposited each year. The Skagerrak acts as a sink for suspended matter transported by inflowing currents. Approximately 17 million tonnes of suspended matter comes annually from the North Sea (Eisma and Kalf, 1987). The major currents are believed to influence the spatial distribution of contaminants within these areas, although most contaminants derived from Scandinavia are trapped in the coastal zone (Cato, 1997a).

Except for a few minor subareas close to point sources, the study area does not show any sign of heavy contamination (Magnusson et al., 1996). Sæther et al. (1996) found that the sediments in the Norwegian part of the Skagerrak could be classified as fair with respect to Ni and Pb and good with respect to Cr, Cu and Zn.

4. Data

Between 1987 and 1992 the Geological Survey of Sweden made a thorough hydroacoustic investigation and sampling of the Kattegat/Skagerrak sediments, mainly within the Swedish economical zone. This was made within the framework of the Swedish Marine Geological Mapping Program and aimed at describing the sediment characteristics, conditions and dynamics in this area. The sediment samples were collected using both box-corer (Jonasson and Olausson, 1966) and gravity corer (Niemistö and Voipio, 1981). The samples were freeze-dried and stored in plastic boxes before analysis. The metal analysis was carried out using the XRF-technique and ICP-MS. In the latter, 0.125 g of the sample was fused with 0.375 g $LiBO_2$ and dissolved in HNO_3 before using the ICP-MS. XRF was mainly used for the sediments in the southernmost Kattegat, whereas the ICP-MS was adopted for the entire area. Although XRF does not give the same precision as ICP-MS, there are no significant differences as both methods were used to analyse the total amounts in the samples. This was controlled by

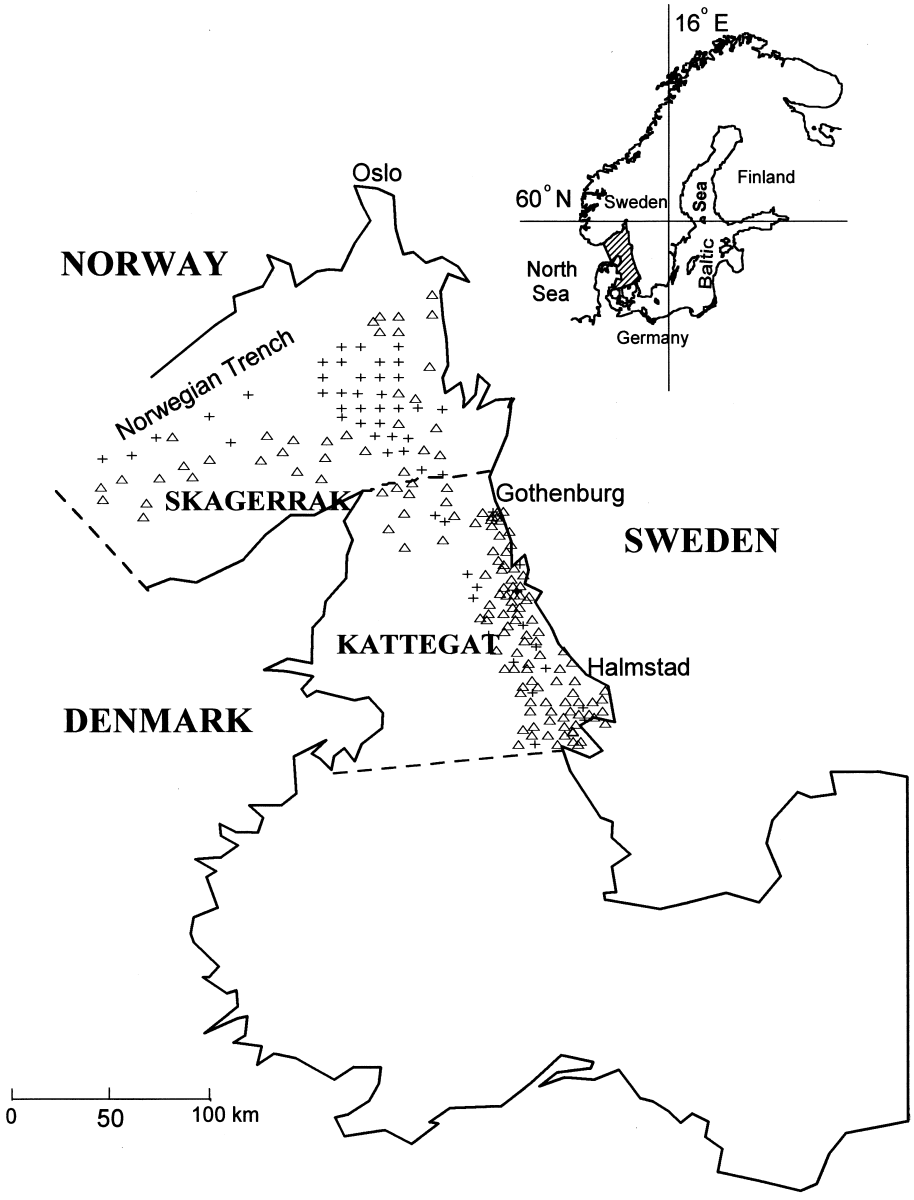

Fig. 1. The study area with stations (+ denotes stations also included in the deep sediment comparison).

comparing stations analysed by XRF with geographically close stations analysed by ICP-MS.

The main part of the data comes from the top layer (0–2 cm) of the sediments. Although the deposition rates differ substantially, this sediment layer can be regarded as representing the last decade, i.e., the 1980's (Kuijpers et al., 1993).

Ten metals were of interest; Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn. To see if the variations in concentrations were due to anthropogenic influence or some diagenetic processes the metals were normalised by using Al, a procedure recommended by e.g., Owens and Cornwell (1995) and Borg and Jonsson (1996). Aluminium is assumed to be a conservative element compared to anthropogenically affected metals like Pb (Salomons and Förstner, 1984).

Copper and Mo included censored data, i.e., values below the detection limit. For Cu the censored data (13 observations) was replaced with values drawn randomly from the left tail of a truncated normal distri-

bution (i.e., between zero and the detection limit), see Helsel (1990) for a description of the procedure. As Mo only held one censored observation this procedure seemed unnecessarily laborious and the censored data was replaced by half the detection limit. This is a fairly common treatment and even though it does not have a theoretical basis it may be used to replace one single observation (e.g., Helsel and Hirsch, 1992).

Additionally, a comparison was made with the deeper sediments. These sediment samples were from 50–55 cm below the surface layer. This layer is assumed to have been formed before industrialisation. Of the 76 deep sediment samples only 54 were used, as the others did not have corresponding surface samples (Fig. 1). Boxplots for the surface and subsurface metals are shown in Fig. 2a–k. To reduce the influence of different ranges of concentration, the normalised concentrations were standardised before statistically analysing them.

5. Results

In this part, results from the PCA are shown and briefly discussed with the results from the clustering. Finally, a comparison with the deeper sediments is given.

5.1. Principal Component Analysis

PCA can only be used successfully for data reduction if the ingoing variables are highly correlated. In Table 1 Pearson's correlation coefficient for the surface concentrations are presented. As seen, most metals are moderately correlated. This cannot be seen as a result of anthropogenic influence, as the correlation structure is similar (although slightly higher for most combinations) to the one found for the subsurface layer (Table 2). Another method was to log-transform the data to reduce the effect of high variation in the variables, before the correlation was calculated (cf. Sæther et al., 1996). This slightly improved some of the correlations, but the main situation was the same. To conclude, no external factors for the low correlations were detected, and therefore they are assumed to be typical for this area.

When doing a PCA, with varimax rotation, it was seen that 3 components (eigenvalue >1) explain 71% of the total variance. In Table 3 the factor loadings for the components are shown.

Cadmium, Co, Fe, Pb and Zn concentrations mainly describe component one, while component two depends strongly on Cu, Mo and Ni. The third component increases with Mn concentrations and slightly decreases with Cr concentration. Fig. 3a–c shows the spatial distribution, using linear interpolation, of the respective component.

5.2. Cluster analysis of principal components

Doing cluster analysis on the principal components additional information of the interaction of sampling stations was gathered. Less well-separated clusters will generate different outcomes for different cluster algorithms. To see if the clustering was fairly robust, different clustering procedures were tested (average, complete, centroid, density, furthest neighbour, McQuitty and Ward's clustering). No major differences were found. In fact, most of them gave if not equal then at least similar results to what was found for average and Ward's clustering. In addition, different distance measurements were tested (Euclidean, Pearson's correlation, block and Chebychev). The major features were identyfied by the different measurements and it was therefore decided to use the common squared Euclidean distance.

The dendrogram shows that 5 clusters are reasonable for Ward's clustering (Fig. 4). It also revealed that clusters 1 and 2 are more likely to join than any of the other three. The five clusters were chosen to represent the classes used in further analysis of the components. The two largest clusters, 1 and 2 (101 and 89 stations, respectively) are mainly geographically situated south- and northwards, although some 'mixing' can be seen. Cluster 3 and 4 (found in the Skagerrak) have two stations each, while cluster 5 only includes one. Of these 3 clusters, at least number 5, located right outside the city of Halmstad, is due to a point source.

The dendrogram, for average linkage of components, reveals that most stations are grouped together at an early stage and that five clusters are reasonable also here. The picture is very similar to what was found in Ward's clustering. The two large clusters (1 and 2) in Ward's analysis now form one large cluster. Cluster 3 and 5 are identical, while the two stations in Ward's cluster 4 are split into two separate clusters.

5.3. Cluster analysis of metals

As a complement to the principal components, the clustering was also done directly on the metal concentrations (normalised and standardised).

Large clusters are formed at an early stage in Ward's clustering of the metals and the pattern is similar to the one found for average linkage of principal components. The main difference is that cluster 3 was found in the Norwegian trench (11 stations), which was not detected in the clustering of principal components (Fig. 5).

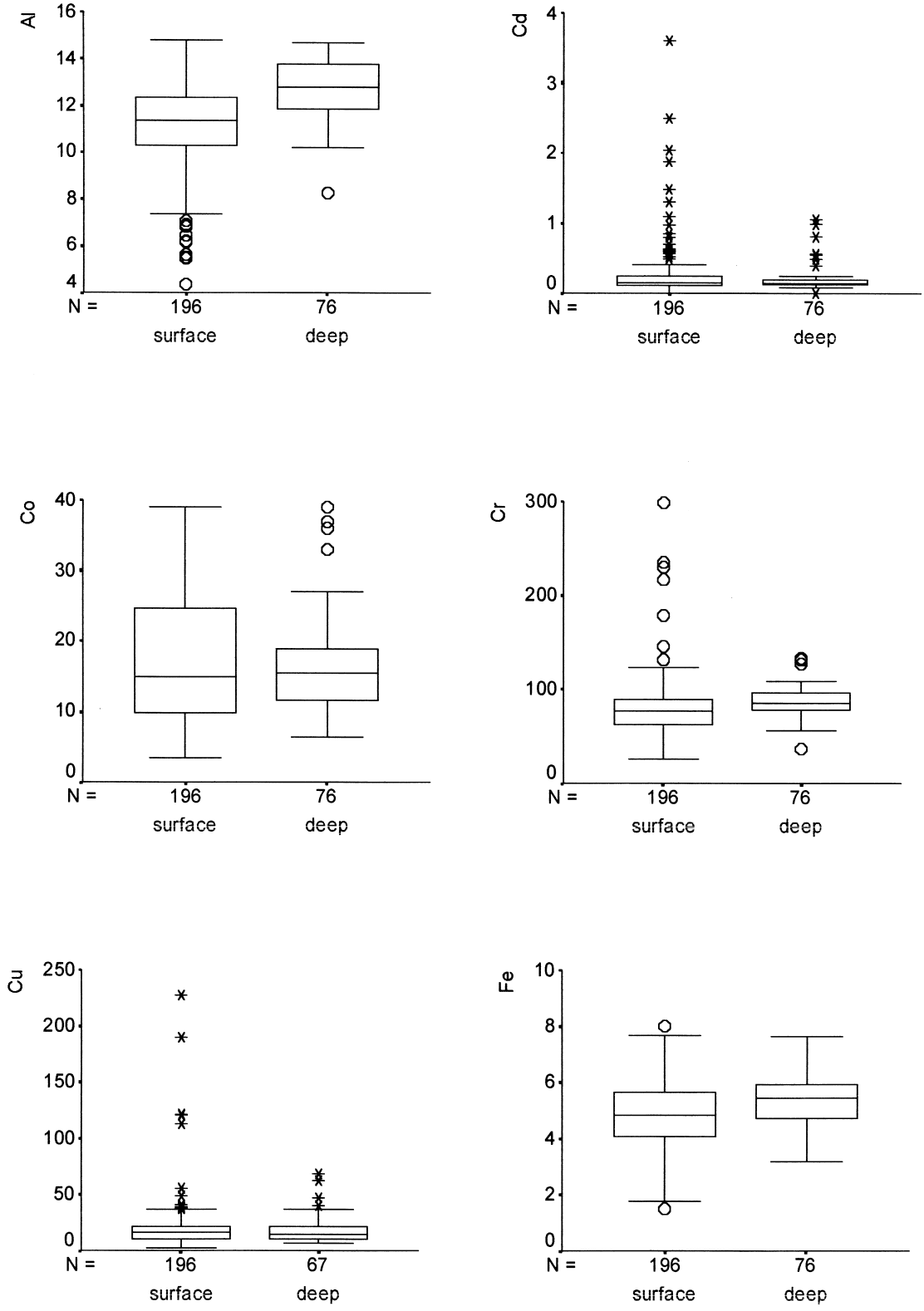

Fig. 2. Boxplots for the metals in the surface and deep layer. Concentrations in mg kg^{-1}, except Al, Fe and Mn which are in g kg^{-1}. a) Al; b) Cd; c) Co; d) Cr; e) Cu; f) Fe; g) Mn; h) Mo; i) Ni; j) Pb; k) Zn.

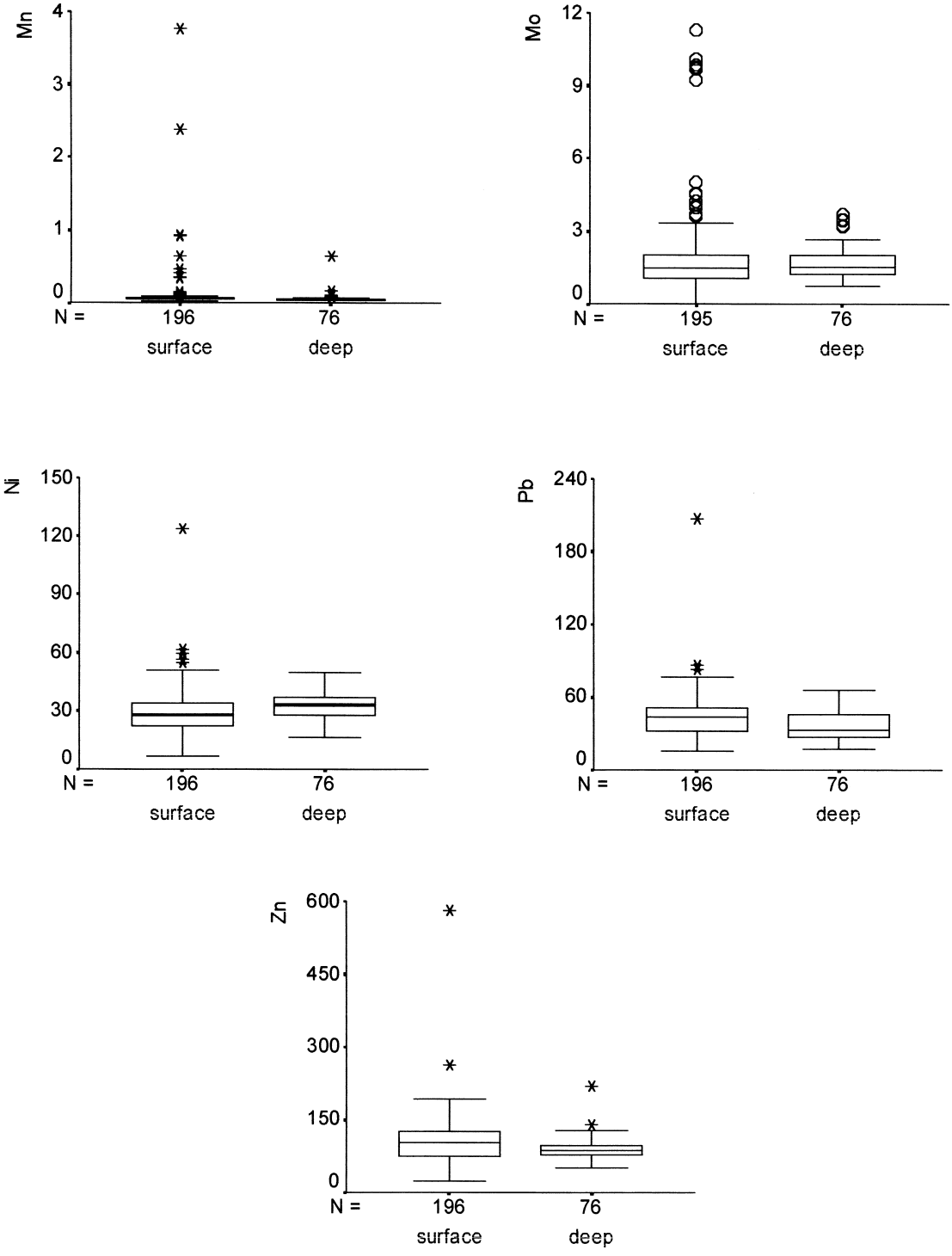

Fig. 2 (*continued*)

Table 1
Pearson's correlation coefficients between normalised metals in the surface layer

	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
Cd	0.22	−0.13	0.06	0.12	−0.04	0.35	−0.04	0.15	0.34
Co		−0.04	−0.02	0.46	0.08	−0.02	0.24	0.62	0.55
Cr			−0.09	0.01	−0.09	−0.11	0.15	0.20	−0.08
Cu				−0.01	−0.07	0.04	−0.03	−0.08	−0.01
Fe					0.24	0.00	0.51	0.47	0.49
Mn						0.18	0.35	0.24	0.01
Mo							−0.07	−0.18	−0.05
Ni								0.51	0.41
Pb									0.73

Like clustering of components average linkage clustering of metals gives almost the same picture as Ward's clustering of metals. Also the main differences are the same, Ward's cluster 1 and 2 now form one large cluster. Compared to the average linkage of principal components a cluster in the Norwegian trench is found.

As in the former case of clustering of components, the spatial distribution of cluster from average linkage is similar to the one of Ward's clustering. Apparently cluster 1 is dominating most of the area and clusters 3, 4 and 5 only embrace one station each.

In Fig. 6a–c the 3 principal components are plotted with information from Ward's clustering of metals. Cluster 1 is mainly kept on the positive side of component one, while both clusters 2 and 3 are found on the negative side. As for component 2 it is seen that most stations have negative values, disregarding cluster identification. Whereas cluster 3 has strongly negative values for component 3, both clusters 1 and 2 are evenly spread around zero.

Table 2
Pearson's correlation coefficients between normalised metals in the subsurface layer

	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
Cd	0.22	−0.16	−0.02	0.29	0.06	0.49	0.04	0.14	0.49
Co		0.07	−0.11	0.53	0.23	0.06	0.29	−0.22	0.07
Cr			−0.14	0.49	0.18	−0.13	0.68	0.56	0.41
Cu				−0.12	−0.05	−0.04	−0.23	−0.19	−0.16
Fe					0.44	0.17	0.84	0.11	0.28
Mn						0.04	0.41	−0.07	0.00
Mo							−0.08	0.07	0.22
Ni								0.26	0.27
Pb									0.75

Table 3
Factor loadings for the first three principal components

Variable	PC 1	PC 2	PC 3
Eigenvalue	3.47	2.46	1.17
Cd	0.754	0.080	−0.059
Co	0.672	−0.076	0.043
Cr	0.159	0.016	−0.566
Cu	0.056	0.864	−0.265
Fe	0.734	−0.052	0.245
Mn	0.123	0.226	0.816
Mo	−0.072	0.875	0.178
Ni	0.069	0.866	−0.091
Pb	0.923	0.155	−0.074
Zn	0.922	0.176	−0.047

5.4. Cluster separation

To find which metal separates the different clusters, Tukey's multiple comparison test for mean values was adopted (see e.g., Helsel and Hirsch, 1992).

Only clusters 1 and 2 (101 and 89 stations, respectively) from the PCA were used, as the other three were too small. The larger of the two have significantly higher concentrations for all metals except Cr, Cu and Mo, where no significant differences were found. Remarkably large values for component 3, 2 and 1 define clusters 3–5, respectively.

For the metals, clusters 4 and 5 were not included in the pairwise tests, as they had too few stations (two and one, respectively). Table 4 presents results from the pairwise tests. Cluster 1 has significantly higher mean concentrations than cluster 2. Exceptions are Cu, Mn and Mo where no significant differences are detected. Compared to cluster 3, cluster 1 has significantly higher concentrations for Cd, Co, Fe and Zn.

Nickel shows an interesting pattern. Clusters 1 and 2 significantly differ from each other but neither of these clusters is significantly different from cluster 3, which can be seen as an intermediate.

The metal separating cluster 3 from the other two is Cr, as the concentration is significantly higher. Looking at the two clusters not included in the Tukey's test it is seen that cluster 4 includes high Cu, Mo and Ni concentrations, while cluster 5 has high concentrations of Cd, Co, Fe, Pb and Zn.

5.5. Subsurface sediments

As the subsurface layer only includes measurements on a fraction of the surface layer locations the boxplots are not directly comparable. Instead a paired *t*-

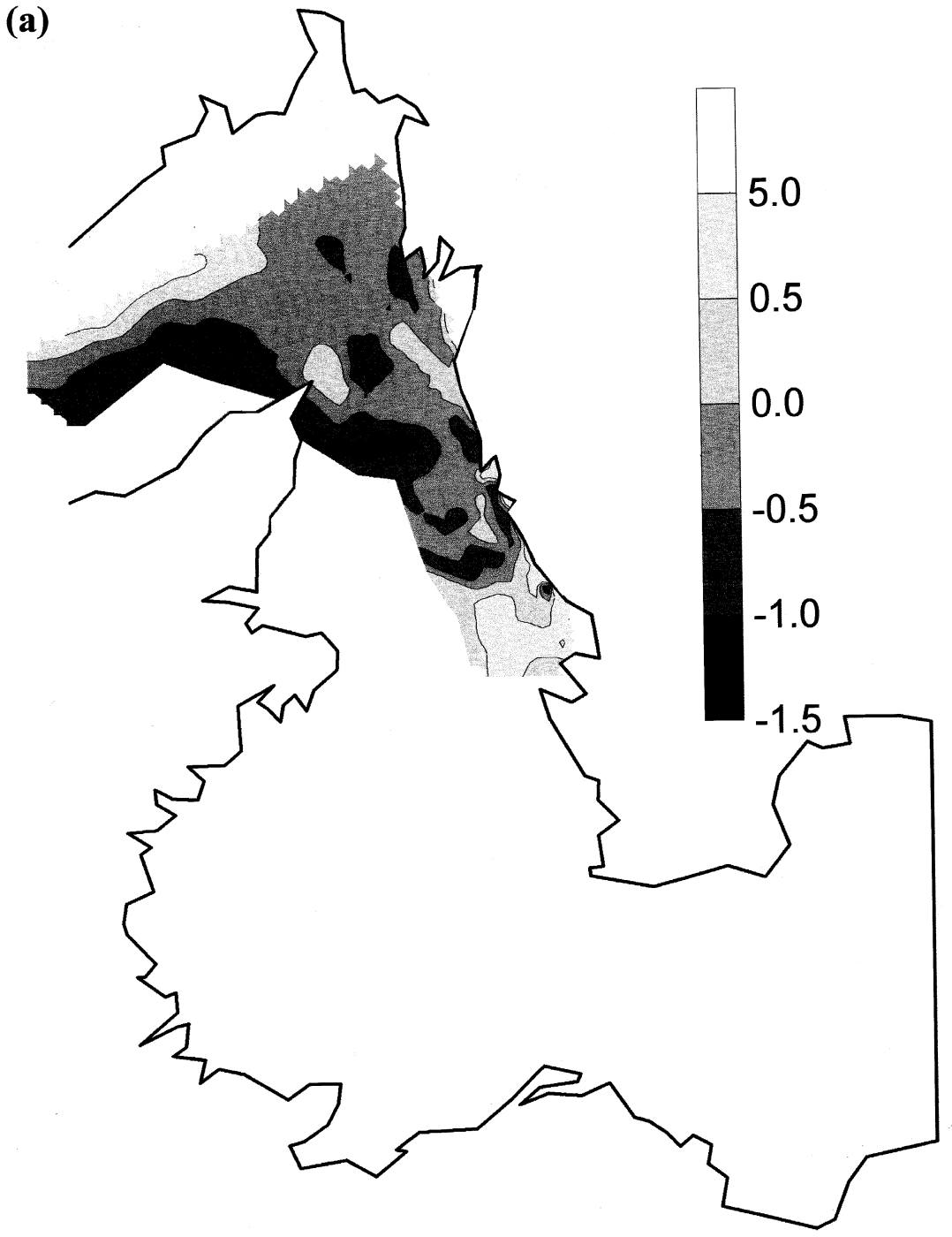

Fig. 3. Geographical distributions of principal components. a) PC1; b) PC2; c) PC3.

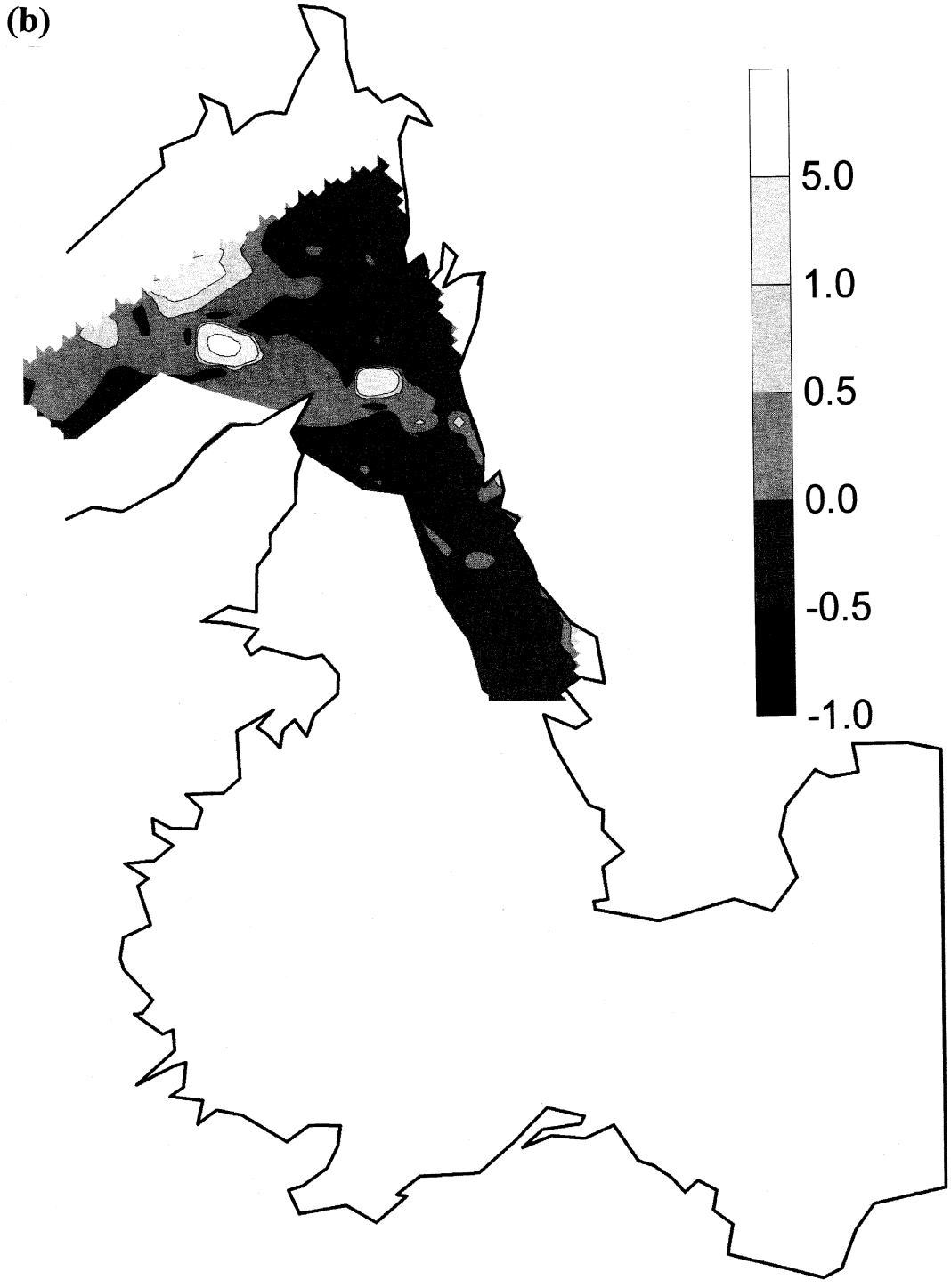

Fig. 3(b). (*continued*).

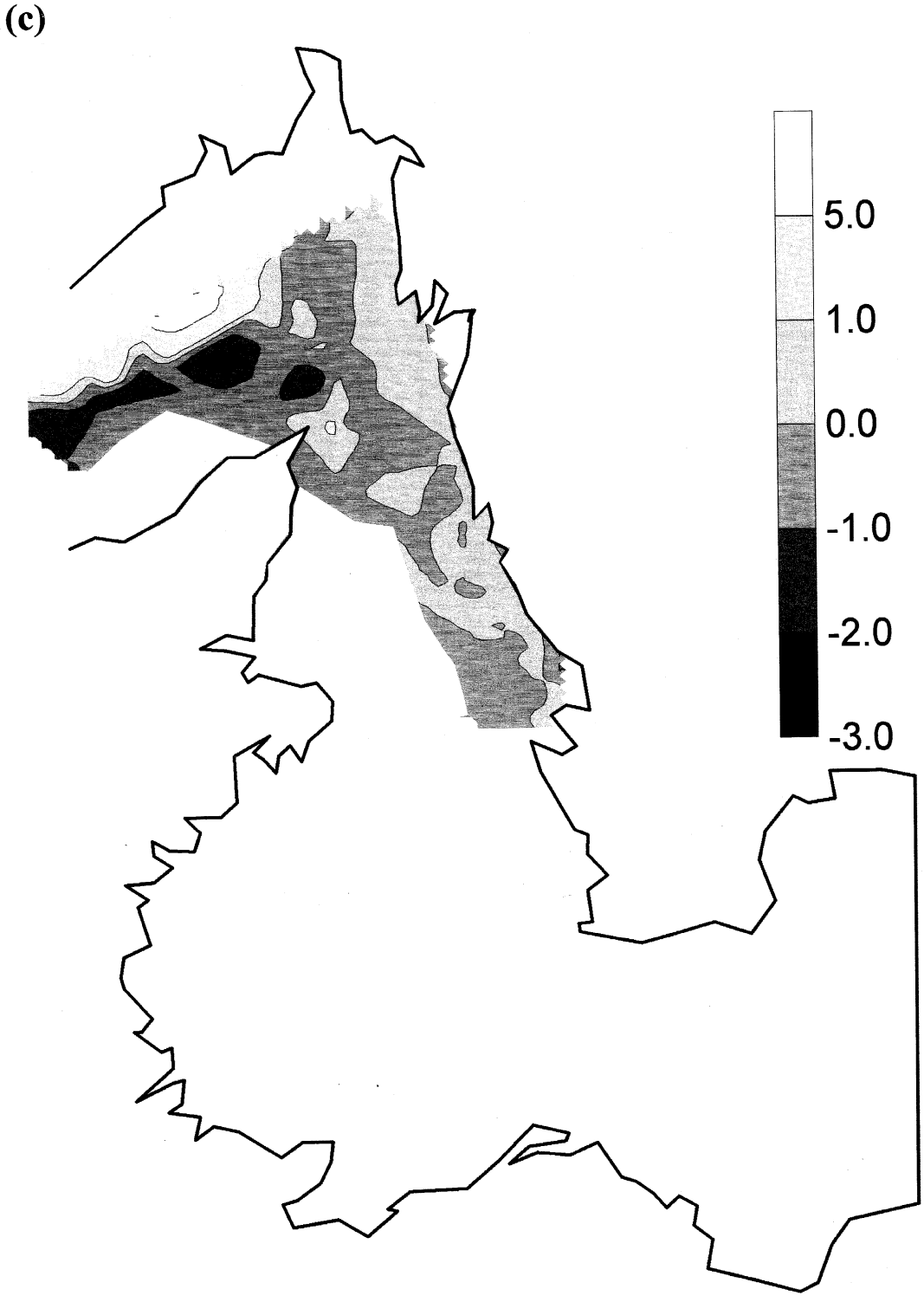

Fig. 3(c). (*continued*).

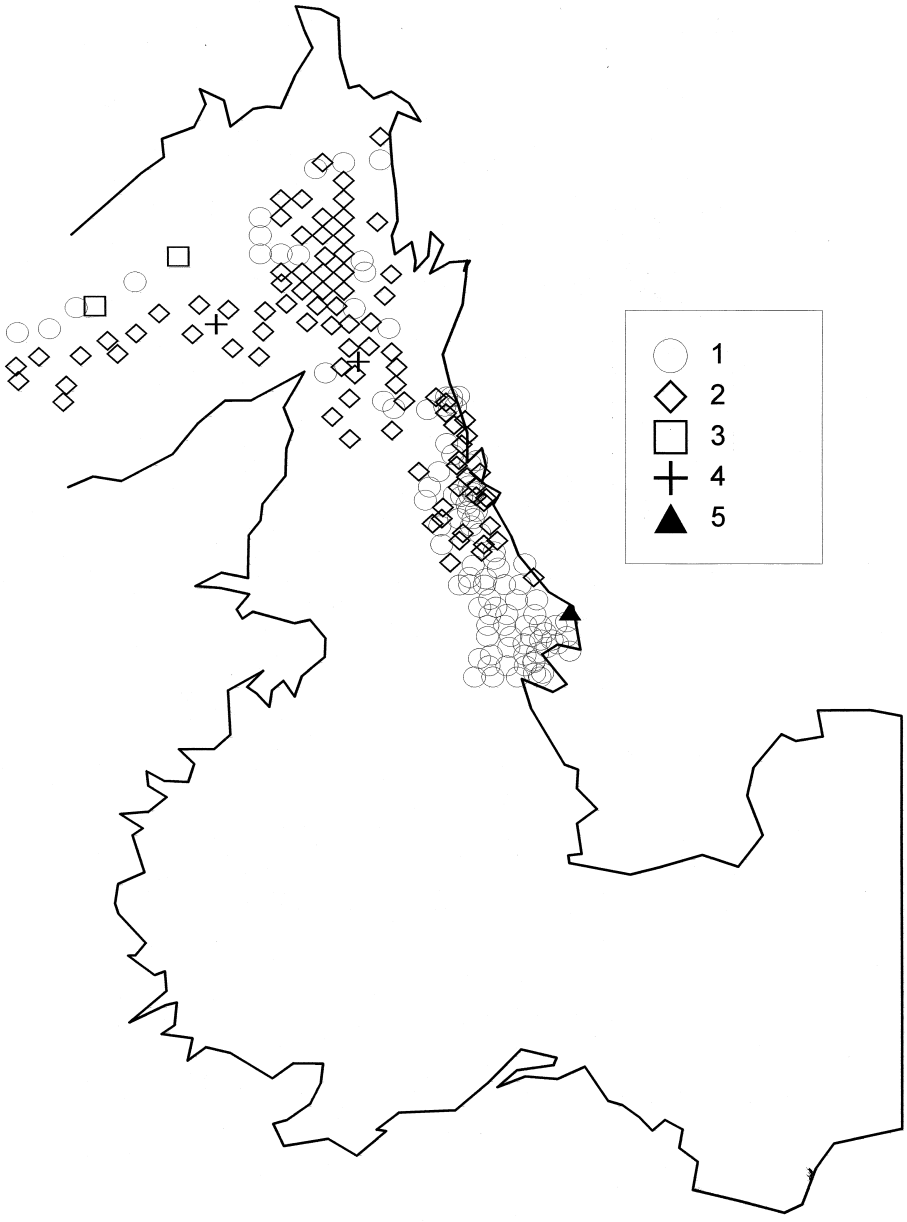

Fig. 4. Geographical distribution of Ward's minimum variance clustering of PC.

test was used to reveal significant differences between the metal concentrations in the subsurface (50–55 cm) compared to the surficial sediments (0–2 cm). This test was adopted on each metal separately. To see if the assumption of normality was fulfilled, histograms of the differences were studied. They could all be seen as approximately normally distributed (not shown). The only significant differences found, at a significance level of 5%, were increased concentrations of Pb and decreased concentrations of Al and Cr (Table 5). The increases in Mn and Zn are almost significant.

6. Discussion

The multivariate methods used are critizised for the difficulty in interpreting results. In cluster analysis, the

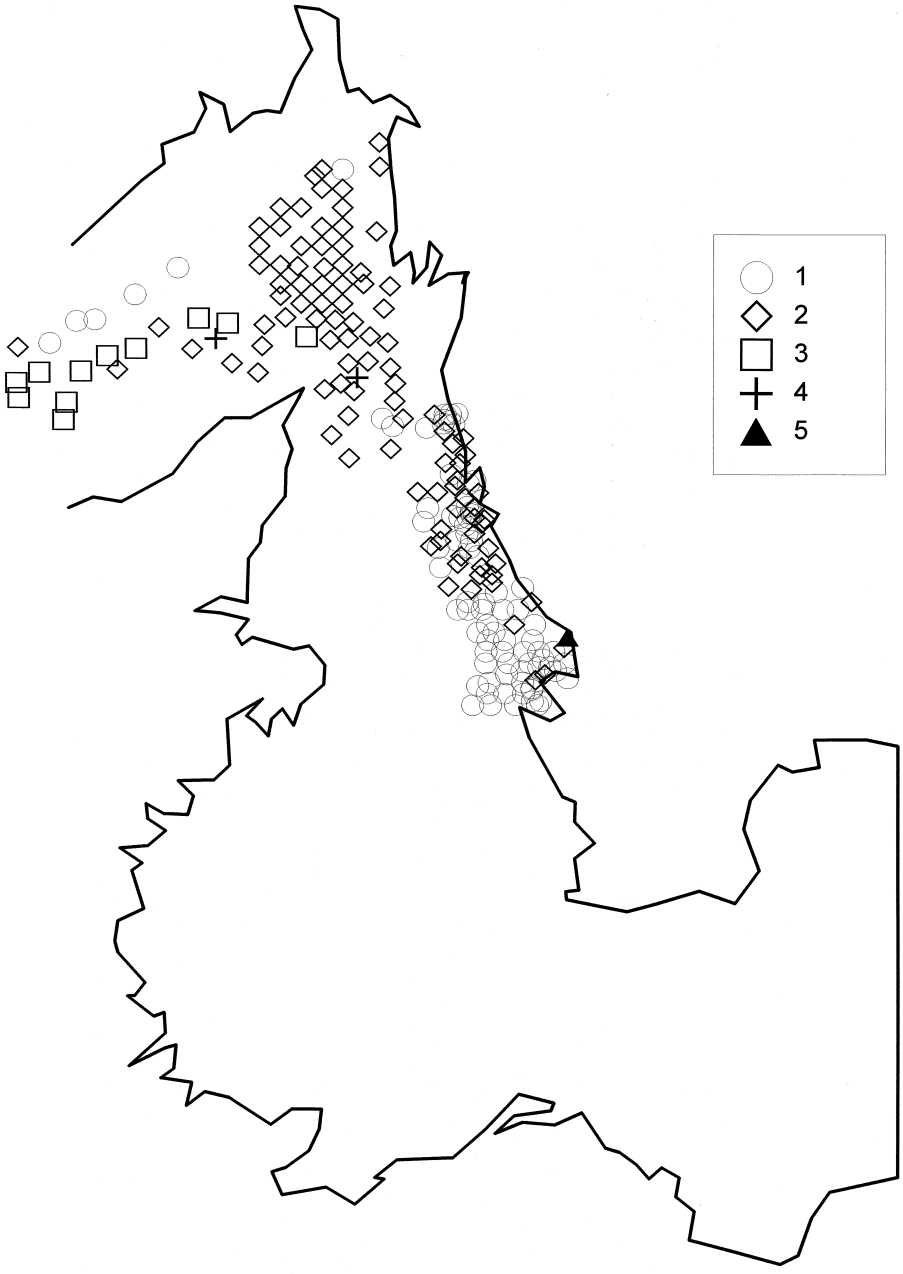

Fig. 5. Geographical distribution of Ward's minimum variance clustering of metals.

question of subjectivity has been risen (see e.g., Griffiths, 1987). It has also been questioned if the obtained cluster results are due to the method and not the data. In this study, as mentioned above, different methods give essentially the same picture. As the patterns obtained from the different cluster setups (average, Ward's, PC and metals) were all very similar this can be seen as an indicator that the clusters are rather consistent and well separated.

In addition, most clustering methods include some bias concerning their ability to detect certain types of clusters and/or in their tendency to form equal sized groups (see e.g., Sharma, 1996). Ward's is biased towards forming equal sized clusters, while average

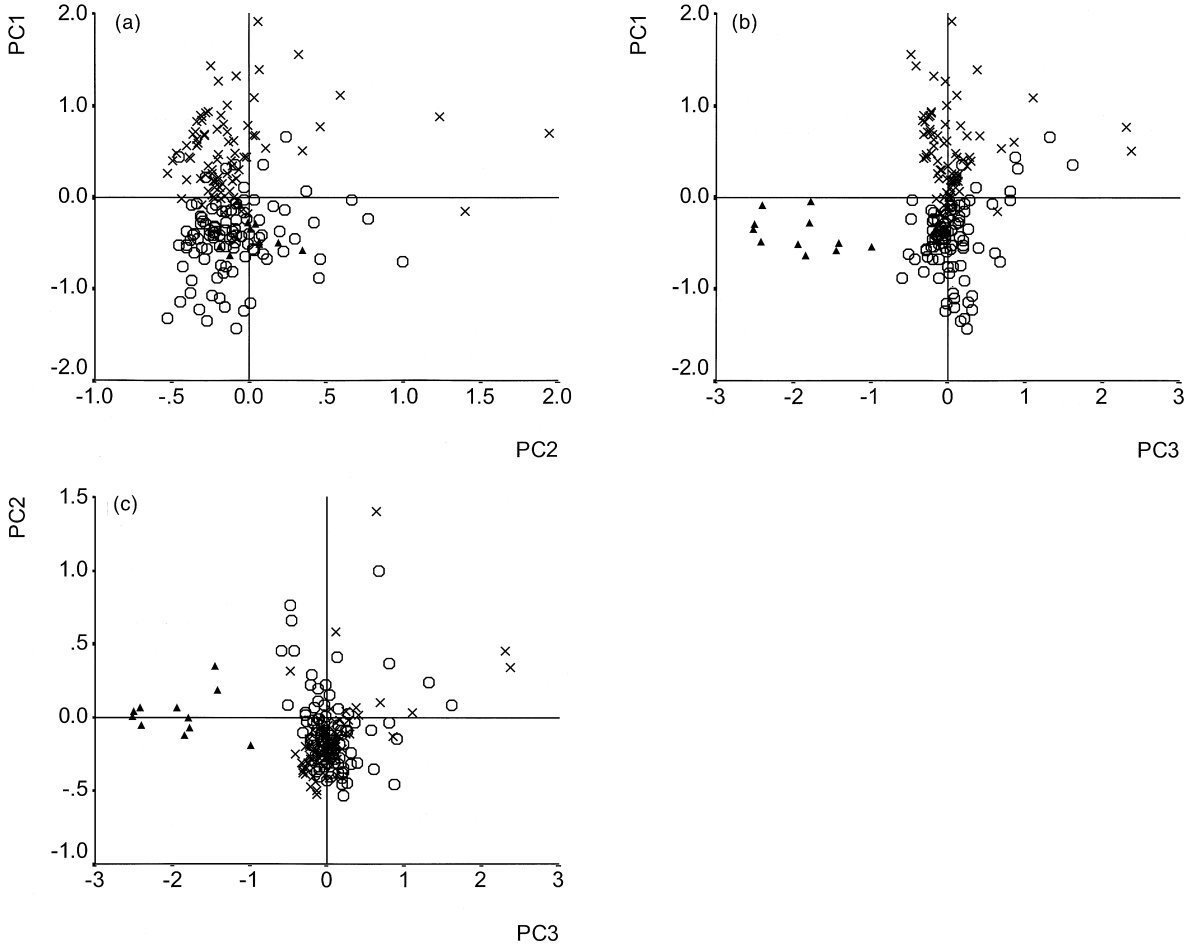

Fig. 6. Principal components, with cluster identification as markers (× = 1, ○ = 2, ▲ = 3). a) Component 1 versus 2; b) component 1 versus 3; c) component 2 versus 3.

linkage form clusters with similar variances. Neither of these shortcomings seems, however, to be valid in this study.

The first component, in the PCA analysis, exhibits high positive weights for Cd, Co, Fe, Pb and Zn. It is well known that Fe, in aerobic conditions, quickly precipitates as insoluble Fe oxyhydroxides (Drever, 1997). The flocculation of Fe is even more pronounced when freshwater enters saline water with an increase in ion strength (Görlich et al., 1989; Szefer et al., 1993). It is also known that one main mechanism for several trace metals, such as Zn, Pb and Cd, is the co-precipitation with the Fe oxyhydroxides (Salomons and Förstner, 1980; Bryan and Langston, 1992; Szefer et al., 1995). Thus, the results for component one are in accordance with earlier findings regarding the ability of Fe oxyhydroxides to co-precipitate with certain trace metals.

Copper and Ni and occasionally Mo have been suggested to relate to the settling and dissolution of biogenic material (Sclater et al., 1976; Bruland, 1980; Shaw et al., 1990; Coveney et al., 1991). Component two exhibits high factor loadings for these metals, which may indicate variations in biogenic productivity. However, these metals must after deposition at the sediment surface be preserved within the sediment in order to be a useful indicator of productivity. The surface sediments in this study are commonly oxidised and will scavenge Cu and Ni efficiently after deposition (Shaw et al., 1990). The oxidised form of Mo is less stable than its reduced form (Shimmield and Price, 1986) and is commonly used as a productivity marker in reduced environments (Wilde et al., 1989 and Coveney et al., 1991). It has also been used as an indicator due to its involvement in N-fixation (Rueter and Petersen, 1987).

Component 3 exhibits a high factor loading of Mn,

Table 4
Tukey's multiple comparison test ($\alpha = 0.05$). Clusters with different letters show a significant difference between them, for respective normalised metal

Variable	Cluster 1	Cluster 2	Cluster 3
Cd	A (0.04)	B (0.02)	B (0.01)
Co	A (2.08)	B (1.12)	B (1.10)
Cr	A (6.84)	B (6.26)	C (21.10)
Cu	¯ (1.49)	¯ (1.79)	¯ (1.14)
Fe	A (0.47)	B (0.40)	B (0.38)
Mn	¯ (0.01)	¯ (0.01)	¯ (0.01)
Mo	¯ (0.17)	¯ (0.16)	¯ (0.13)
Ni	A (2.73)	B (2.32)	A,B (2.38)
Pb	A (4.42)	B (3.27)	A (3.95)
Zn	A (11.03)	B (7.37)	B (6.54)

¯ = No significant difference. Number in parenthesis is the mean concentration.

which suggests that none of the trace metals are associated to the Mn distribution. This was expected since Mn is continuously mobilised from the deeper reduced part of the sediments into the interstitial waters. From there it migrates upwards to the oxidised surface layer where an enrichment takes place (Förstner and Patchinelam, 1976). Due to the very low solubility products of the other metal sulphides they can be considered stable (see e.g., Hallberg, 1973; Loring, 1975). Consequently, they do not follow the Mn cycle.

Of the five metal clusters, the first probably reflects the conclusion drawn about component one, i.e., the trace metals Pb, Zn, Co and Cd co-precipitate with Fe oxyhydroxides in the coastal zone and near their sources, preferably in the Gothenburg and Laholm Bay area. Comparing the results from the PCA and those from the cluster analysis (Fig. 6a) it is seen that the values from cluster one almost exclusively embrace positive factor loadings, i.e., Pb, Zn and Fe dominate in that cluster. Five stations, belonging to this cluster, are found in the deepest part of the Norwegian trench. The process affecting them is probably the same as mentioned above, although their source is geographically different. Also the Mn concentrations are high in this trench.

Table 5
The *t*-ratio and *P*-value come from a two-sided *t*-test between the deep sediments and the surficial ones. A negative *t-ratio* indicates a higher concentration in the surficial sediments

Variable	*t*-ratio	*P*-value
Al	5.99	0.000
Cd	0.92	0.362
Co	1.35	0.181
Cr	3.45	0.001
Cu	−1.02	0.314
Fe	1.57	0.121
Mn	−2.05	0.045
Mo	−1.07	0.291
Ni	1.29	0.203
Pb	−4.89	0.000
Zn	−1.97	0.054

Cluster 2 embraces negative factor loadings and is accordingly dominated by metals with negative or low factor loadings, i.e., Mo, Cu and Ni. Thus, the separation between cluster 1 and 2 is probably due to differences in the affinity between metals in their efficiency to co-precipitation with Fe oxyhydroxides and not an effect of differences in productivity or sources. The results from the PCA distinguish between metals with high affinity to Fe oxyhydroxides and metals influenced by alteration in the productivity or their affinity to organic matter, i.e., the variation in sedimentary organic matter content. Consequently, the metal pattern with high and low concentrations, respectively, of Cu, Mo and Ni seems to indicate variation in biogenic and organic matter load and sequestering capacity. Opposed to this is the lack of Zn in cluster 2, as Zn has a very close and positive relationship to organic C in the Skagerrak area (Cato, 1997b). This relationship has also been found in many other areas (e.g., Gorham and Swaine, 1965; Piper, 1971; Ryding and Borg, 1973). Therefore, other mechanisms governing Cu, Mo and Ni, e.g., differences in the sources of clastic materials, can not be excluded.

Significantly higher concentrations of Cr separates cluster 3 from the other clusters Table 4. This cluster is interesting as its stations are grouped in the southwestern part of the Skagerrak and coincide with the sediment transport along the Danish NW coast from the southern North Sea. According to Bengtsson and Stevens (1996) this transport is one of the most important sources of heavy metals to the Skagerrak. It is most likely that Cr is enriched in these sediments with relatively high contents of minerals like garnet, tourmaline and rutile, suggesting a southern North Sea origin.

The lack of influence of Mn in the clusters is, as mentioned above, explained by its high mobility. High concentrations in the deep Norwegian trench may be due to the low sedimentation rates (<1 mm a^{-1}) observed in this part of the Skagerrak (cf. the Mn enrichment in deep-sea areas). On the other hand, in the deep anoxic sediments of the Baltic proper, a large variation in Mn concentration is found between otherwise similar sites (Carman and Rahm, 1997).

The somewhat surprising results from the comparison between surface and subsurface sediment layers, where only two elements showed an increase over time, may be an effect of the intense bioturbatation and trawling (Flodérus, 1989). Increasing trends of metals,

due to increased pollution, have been found in the archipelago of the Bohus coast and in the fjords (Cato, 1997b). It would probably also have been seen in the offshore sediments if no mixing had existed. The higher Al concentrations found in the subsurface layers is probably an effect of differences in the clay content, as more clay minerals leads to higher Al concentration.

It has been shown by e.g., Shaw et al. (1990), Hallberg (1991), Borg and Jonsson (1996) and Brügmann et al. (1997), that the redox conditions have a great impact on the spatial distributions of metals in the sediments. Unfortunately, no data existed on the redox conditions, so this influence could not be investigated.

To summarise, the analyses shed some new light on the spatial distribution of recently deposited heavy metals in a coastal zone area. PCA grouped the different stations according to their chemical composition. It turned out that the different clusters formed distinct patterns in the PCA space. Also, by clustering the metals according to concentration and studying their geographical distribution, distinct deposition patterns were observed. In addition, a significant increase of Pb and Zn and a significant decrease of Al over time was revealed. By all this, the authors hope to have shown the meaningfulness of multivariate statistical methods for analysis of the complex relationships between heavy metals in sediments.

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