C M 1996/R:2

VERTICAL AND SPATIAL DISTRIBUTION OF CARBON AND NUTRIENTS IN THE SOFT BOTTOM SEDIMENTS OF THE BALTIC SEA

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Abstract

The vertical and spatial concentration pattern of carbon, nitrogen and phosphorus in soft bottom sediments from all sub-basins of the Baltic Sea has been investigated. The highest total concentration of carbon and nitrogen are found in the central deep part of the Baltic proper. The concentration at similar bottoms in the Bothnian Bay and Bothnian Sea is about 1.5 to two times lower. The inorganic concentration of carbon is normally far below 1% in the entire Baltic Sea except for some localities with anoxic conditions where autigenic precipitation of mixed manganese carbonates occurs, e.g. eastern Gotland deep. Manganese seems to be of essential importance for such precipitation. The average molar ratio of the precipitate is 0.64 (Mn/C) with a very high coefficient of determination (R^2=0.97). As for carbon, a dominant proportion of the nitrogen found in the sediments is organically bound. The inorganic amount exceeds seldom 10% of the total amount of nitrogen. For phosphorus, on the other hand, a dominant proportion is inorganically bound. The highest total concentrations are found in the eastern part of Gulf of Finland. High concentrations are also found in the well-oxidized sediments of the Bothnian Bay and Bothnia Sea. In these latter areas phosphorus is highly linked to the vertical concentration trends of manganese. The linear coefficient of determination (R^2) between the sediment concentration of manganese and phosphorus is always higher than 0.85 even though the average molar ration (Mn/P) varies between the different sites of that region. The nature of the sediment matrix (grain size, mineral chemistry etc.) combined with oxygen condition depend mainly how and to which extent the incorporation and burial of phosphorus occur. For instance, the inorganic concentration of phosphorus decreases sharply when the sediment turns from oxic to anoxic conditions. This is mainly due to reduction of ironoxyhydroxides which during oxic condition adsorb large amount of phosphorus.

The organic C/N ratio is vertically very stable at each location indicating that the degradation of the organic matter in the sediment proceeds with constant C/N proportionality. There are also small variations in the C/N ratio between different areas of the Baltic Sea even though higher average ratios are found in the northern part of the Baltic Sea. The organic C/P ratio within the sediment departs considerably from the Redfield ratio, mainly due to more or less instant releases of easily hydrosable organic phosphorus molecules.

1. Introduction

The Baltic Sea, which is one of the largest bodies of brackish water in the world, represents a unique environment both in terms of its impoverished fauna and flora, hydrography and biogeochemistry (see for instance Voipio, 1981; Elmgren, 1984; Larsson et al., 1985; Emelyanov, 1988).The Baltic Sea could be divided in three distinct main basins (Baltic proper, Bothnian Sea and Bothnian Bay; Figure 1) which are separated by shallow sills. The southernmost main basin (Baltic proper) could in turn be divided in additionally two smaller basins, i.e. Gulf of Riga and Gulf of Finland). These two latter basins comprise a comparatively small area of the total Baltic proper and have comparably shallower water depth. Further, these two basins are also considered to be the most polluted areas of the Baltic Sea (HELCOM, 1990; Andrushaitis et al. 1992). The two northernmost basins of the Baltic Sea have the lowest salinity (1-3 and 3-7 PSU for Bothnian Bay and Bothnian Sea, respectively) and a weak salinity stratification. The Baltic proper (excluding Gulf of Finland and Gulf of Riga) has a strong halocline located at 60-80 m depth (Kullenberg, 1981) which separate the surface water with a salinity between 7-8 PSU from the deep water with a salinity of 9-20 PSU. Renewal of the deep water to the Baltic proper, through the Belts of Denmark and the Sound, is virtually continuous. However, inflow of high salinity water is mainly the result of certain storm events and large-scale atmospheric distributions and therefore occurs less frequently. The Gulf of Finland has weaker salinity stratification (Perttilä et al., 1995) whereas the Gulf of Riga normally exhibits lack of such stratification. The salinity stratification in the Baltic proper and Gulf of Finland result sometimes in more or less complete oxygen depletion, which in some areas of the Baltic proper is permanent (Jonsson et al., 1990). In these environments microorganisms will preferably use sulfate instead of oxygen in the oxidation of supplied dead organic matter. Subsequent production of hydrogen sulfide eliminate all benthic macro fauna which , in turn, entail formation of laminated sediments. Such lamination has been observed to cover large areas in the Baltic proper (Jonsson et al., 1990) as well as restricted areas in the Gulf of Finland (Morris et al., 1988). Changes in oxygen/redox condition in the water and within the sediment will highly alter the biogeochemical processes. Hence, the fate of supplied carbon and nutrients to the sediment surface will change in different degree as a result of altered diagenetic processes.

Presented investigation is a sub-investigation within a project planned and organized by the ICES Working group on Baltic Marine Environment: Sediment Baseline study. The overall goal of the ICES/HELCOM Baltic Sea sediment baseline study was to assess the use of sediments as environmental indicator medium and, if so, suggest possible sedimentation sites for future environmental monitoring studies. Within the baseline study measurement of sedimentation rates, trace element and nutrient characterization and distribution patterns in the surface sediments will be covered. The aim within presented sub-study is to characterize the carbon and nutrient chemistry with respect to spatial and vertical distribution patterns at these deep accumulation bottoms but also to scrutinize if there are any couplings with the concentration trends with analysed trace metals.

2. Materials and methods

During the sediment baseline study all together forty-two soft bottom sediment cores were sampled during one mount in summer 1993. However, since several of the sampled sediment cores were collected very close to each other only thirty-two sampling sites are examined in this study (Figure 1 and Table 1).The sediments were collected by the use of a Gemini gravity corer which are equipped with two parallel acrylic liners with an inner diameter of 80 mm. The sediment cores were sliced on board the ship in centimetre slices normally down to at least 25 cm below the sea floor (Table 1). The sediment slices were directly put in a deep-freezer and after that freeze dried for measurement of the water content (WC %). Before the chemical analyses the sediment was ground to fine powders in an agate mortar.

Sub-samples were taken for total C, N and P analyses and for different subfractions of these elements. Total carbon (TOT-C) and nitrogen (TOT-N) was measured on a Leco element analyser with a precision of ± 0.5%. Organic carbon (ORG-C) was determinated on pretreated sediment samples with 1 M HCl in the same element analyser (Hedges and Stern, 1984). Inorganic carbon (IN-C) was obtained from difference between the total and organic carbon values. Fixed nitrogen (FIX-N) and exchangeable nitrogen (EX-N) was measured only on selective sites down to a maximum depth of 5 cm below sea floor according to the method described by Silva and Bremner (1966) and Mackin and Aller (1984), respectively. Organic nitrogen (ORG-N) was obtained from differences between the total and the sum of FIX-N and EX-N. All wet extracts of N were measured according to Parson et al. (1984). Total phosphorus (TOT-P) and inorganic phosphorus (IN-P) was measured according to Froelich et al. (1988). Mobile phosphorus (MOB-P) was measured according to Carman and Jonsson (1991) without pretreatment with other chemicals. Apatite phosphorus (AP-P) was obtained from the difference between IN-P and MOB-P whereas the amount of organic phosphorus (ORG-P) in the sediment was obtained by the difference between TOT-P and IN-P. All wet extracts of P were measured using standard spectrophotometric technique (e.g. Murphy and Riley, 1962). Transition and trace metals in the sediments have been analysed by using ICP-AES technique.

3. Results and discussion

3.1 Carbon

The spatial distribution of total carbon in the Baltic Sea is shown in Figure 2. Most of the carbons in the sediments of the entire Baltic Sea are in organic form. This is mainly due to that inorganic carbonates (e.g. calcium carbonates) are unstable in the water mass (e.g. Carman and Rahm, 1996) which result in dissolution of sedimented biogenic as well as abiogenic carbonates. Normally constitute the inorganic part for less than 0.5 mmol/g (< 1% d.w). In the adjacent Kattegatt (e.g. site 155 and 156; Figure 1) and Skagerack the concentration of inorganic carbonates often exceeds 1% d.w. and represents often a significant proportion of the total carbon content (>30%). Autigenic precipitation of mixed carbonates in the sediments with euxinic conditions of the Baltic proper (eastern Gotland Basin) is a process that has been frequently suggested to occur (Manheim, 1961; Suess, 1979; Jakobsen and Postma, 1989; Carman and Rahm, 1996). Such autigenic precipitation could also be discovered in this study at site 171 (Gotland deep). The precipitation seems to start below 9 cm depths below sea floor (Figure 3). The molar ratio Mn/IN-C of the precipitate is 0.64 (Figure 4) with a very high coefficient of determination (R^2=0.97). Thus, manganese is an important major cation for the mixed autigenic precipitate in this environment. The ratio found in this study is very close to that reported by Jakobsen and Postma (1989) who suggest that the precipitate is a Ca-rhodochrosite in which calcium constitute almost the remaining part of the precipitate. Hence, the prolonged euxinic conditions of the eastern Gotland basin with continuos reduction of manganese oxides together with microbial breakdowns of the organic matter using sulfate, with resulting increases in alkalinity, maintains a perfect environment for autigenic precipitation of mixed manganese carbonates. Relatively high manganese concentrations are also found in the sediments at site 167 and 180. However, even though Jakobsen and Postma (1989) found small amounts of Ca-rhodochrosite in the Bornholm basin (site 167) there is no such excellent correlation between manganese and inorganic carbons as that found at site 171.

3.2 Nitrogen

As for the carbon most of the nitrogen in the sediments of the Baltic Sea is organically bound although Müller (1977) shows that the concentration of inorganic nitrogen (fixed and exchangeable; FIX-N and EX-N, respectively) in some areas of the Baltic Sea are much higher than in most other marine areas. Hence, the spatial distribution pattern of total as well as organic nitrogen follows very closely the distribution pattern of carbon (Figure 2). Inorganic nitrogen is reported to be adsorbed on minerogenic particles (preferably on clay minerals) and organic matter in two different ways (e.g. Rosenfeld, 1979), namely as exchangeable ammonium (EX-N) and as fixed ammonium (FIX-N). While EX-N is adsorbed through an ion exchange reaction on the surface of certain organic or mineral surfaces, FIX-N is incorporated in the sediments through adsorption within the clay structure and not easily replaced by other cations. In soft bottom sediments constitute the sum of these two inorganic phases seldom more than 10% of the total nitrogen content of which FIX-N comprises the dominant proportion. However, even though they often represent a minor fraction theirs concentrations could not be disregarded when, for instance, investigations of alterations in organic C/N ratios within and between different sediment environments of the Baltic Sea are performed.

3.3 Phosphorus

In difference to carbon and nitrogen a substantial portion of the phosphorus in the sediment is inorganically bound. Therefore, the spatial distribution pattern (0-1 cm sediment depth) of total phosphorus does not entirely follow that of the carbon and nitrogen (compare Figure 2 and Figure 5). The most obvious difference is that the total concentrations of phosphorus are about the same in the central Baltic proper and the Bothnian Sea whereas the concentration of both carbon and nitrogen are much lower in the Bothnian Sea than in the central part of the Baltic proper. Further, the high coefficient of determination between both the total and the organic content (Figure 10) of carbon and nitrogen at each site of the Baltic Sea does not exist for carbon/nitrogen against phosphorus. The main reason for such a distribution pattern is that the degradation of the organic matter with respect to carbon/nitrogen versus phosphorus occurs in different ways, e.g. the utilization of phosphorus during decomposition of organic matter is independent of the concentration of carbon and seems in difference to carbon unaffected of variations in sedimentation rates (Froelich et al., 1982; Ingall and van Cappellen, 1990).

Inorganic phosphorus constitutes seldom for less than 50% of the total amount and the percentage of inorganic phosphorus at certain deposition bottoms could sometimes comprise up to 90% of the total amount of phosphorus. The corresponding values for carbon and nitrogen are ≤ 5% and ≤ 10%, respectively.

The nature of the sedimentary matrix (grain size, chemistry etc.) combined with redox condition depend how and to which amount the burial of P occurs. Due to low concentrations and often x-ray amorph phases preclude to a large extent direct identification of pure mineral phases. Therefore, a common and often the only way to interpret possible and dominating incorporation mechanisms and to quantify the buried amount of different more or less exclusive phosphorus fractions in the sediments are the use of different sequential leaching procedures (e.g. Williams et al., 1967; Balzer, 1986; Carman and Jonsson, 1991; Ruttenberg, 1992).

The iron cycle is well known to be important for the redox dependant sequestering/release of phosphorus. In the oxic zone large amounts of phosphorus adsorbs too solid ferric complexes. When those complexes' dissolves in the reduced zone they will consequently also liberate the adsorbed amount of phosphorus. It could clearly be seen from the sites in the central part of the Baltic proper (e.g. site 171, 176, 179 and 180). At these sites low concentration of redox dependent phosphorus occurs in the entire sediment profile due to redox values below +230mV (redox cline). Figure 5 (a plot from site 167; Bornholm deep) reveal plainly the quick release of phosphorus from the sediment when the sediment turns from oxidized to reduced condition. In the oxidized zone the concentration of mobile phosphorus is high. However, it succeeds quickly by decreasing concentrations in the hypoxic (100-200 mV) section of the sediment profile and by concentrations close to zero in the reduced zone below 6 cm.

The remaining inorganic amount of phosphorus in the sediment embraces different kinds of apatite phases (Ruttenberg, 1992) but also phosphorus tied up to other minerogenic particles (e.g. clay) and other cations than calcium and iron(III), e.g. aluminium, manganese, iron(II) (Froelish et al., 1982). Manganese seems, as it obviously is for autigenic carbonate precipitation, to be of great importance for precipitation of autigenic phosphates in the northern part of the Baltic Sea (Figure 7 and 8). Figure 7 display nicely that the vertical concentration trends of total phosphorus and manganese are linked to each other in sediment sections exceeding 4 cm depths below sea floor at both site 193 and 195. In that part of the sediment profile a high linear coefficient of determination (R^2) between these parameters occurs (0.84 and 0.86 for site 193 and 195, respectively). However, the molar ratio between phosphorus and manganese differs between these two sites (Figure 8). We can also see similar trends between manganese and phosphorus from sites in the Bothnian Sea (190 and 192), even though the coefficients of determination between phosphorus and manganese are lower at these sites. In the sediments from the Baltic proper (including Gulf of Finland and Gulf of Riga) there is no such pronounced correlation between phosphorus and manganese, although the common main trend is that their concentrations coarsely increase simultaneously. The sediments from the bights in the entrance to the Baltic (site 157,159 and 160) differ completely from the general trends found in the other areas of the Baltic Sea. At these sites the concentration trends of manganese and phosphorus exhibits a relatively good inversely proportional to each other (Figure 9). Obviously, the differences in the biogeochemical environment between the northern part (Bothnian Sea and Bothnian Bay) and the middle and the southern areas of the Baltic Sea affect the burial of phosphorus, carbon and manganese. The far better redox condition in the Bothnian Bay and the Bothnian Sea than what is common at most soft bottom sediments in the Baltic proper, entails that both manganese and iron oxid- hydroxides preserve deep down in the sediment column. This situation with high abundance of metal oxides (mostly as nodules with high contents of manganese; Ingri, 1985) may explain the close connection between phosphorus and manganese as shown in Figures 7 and 8. In the Baltic proper, on the contrary, where the oxygen conditions even in the uppermost part of the sediment often exhibits reduced conditions leads to the dissolution of iron and manganese oxide-hydroxides. The resulting increase in concentrations of these elements in the pore water combined with increasing alkalinity, due to a microbial breakdown of the organic matter using sulfate instead of oxygen as electron acceptor, results demonstrably in autigenic precipitation of mixed manganese carbonates (see previous discussion and, for instance, Jakobsen and Postma, 1989) and iron sulfides (Bågander and Carman, 1994) rather than precipitation of iron and manganese phosphates and/or adsorption of phosphate on redox dependent metal oxides.

3.4. Redfield ratios

The C_{org}:N_{org}:P_{org} ratio of marine particulate organic matter is quite consistent (Redfield et al., 1963; Copin-Montegut and Copin-Montegut, 1983).The C:N:P ratio of 106:16:1 has since the middle of this century been accepted to be the average organic molar ratio in marine organic matter. However, in the Baltic Sea deviation from Redfield ratio has been reported with C_{org}/N_{org} ratio higher than Redfield i.e., between 7-10 instead of 6.625 (Hendrikson, 1975; Iturriaga, 1979; Shaffer, 1987). The N_{org}/P_{org} ratio is, on the other hand, commonly lower, between 12-14 (Sen-Gupta and Koroleff; 1973), whereas the ratio between carbon and phosphorus usually has higher ratios than Redfield. Shaffer (1987) suggests that the most likely or "best" average value for this ratio in the Baltic Sea and adjacent areas should be around 130. In the interpretation of the C_{org}:N_{org}:P_{org} ratio within sediments it should be remembered that the sediments contain different degrees of old (10 000 - 100 ^{14}C years) allochtonic matter (precipitated humus, particulate land delivered organic remnants) with high C/N ratios. However, measured ratios in sedimenting material and in the sediments are important as a base for characterizing the organic matter with respect to the degree of fractionation during decomposition. Fractionation processes during settling and during benthic degradation usually increases the C_{org}/N_{org} and the C_{org}/P_{org} as well as the N_{org}/P_{org}. This is caused by different degree of preferential N and P utilization (e.g. Froelich et al., 1988).

The data presented in Figure 10 represent data from all sites within this study as well as some additional sediment data from similar deposition bottoms sampled in connection with other projects. The average organic C/N ratios from the different sub-basins are given in Table 2. The data represent measurements from the five uppermost centimetres (centimetre sections) of the sediment. As can be seen from Figure 10 exhibits the organic C/N ration a high linear coefficient of determination from all sub-basins of the Baltic Sea, although with different slopes. The C/N ratio in the Baltic proper, Gulf of Riga and Gulf of Finland exhibit almost the same value while the ratio in the Bothnian Sea and Bay are considerably higher (Table 2) . Large supply of fresh water through the many streams in that area with high abundance of terrestrial organic material (e.g. humus) may explain why the C/N ratios in that area are higher than in the southern part of the Baltic Sea. The ratios seem almost independent of water depth, depth below seafloor, carbon content, sediment characteristics and extent of diagenesis within the different basins. Even the topmost section exhibits the same ratio, which suggests that all preferential fractionation (depart from the Redfield ratio) mainly occur prior to settling at the sediment surface or during an early digenetic stage.

The average organic C/P ratio deviates considerably from the Redfield ratio (106:1) in all basins (Table 2). This is mainly a result of preferential instant autolytic release of easily hydrolysable P compounds (e.g. Froelich et al., 1988). Furthermore, besides that the C/P ratios deviating considerably from Redfields, they also exhibit large vertical as well as spatial variations. From presented data it is hard to find a firm explanation for observed trends. However, a combination of differences in sedimentation rates, variation in the amount of supplied terrestrial organic matter and redox condition may explain the large variation in the organic C/P ratios (Froelich et al., 1982; Ingall and van Cappellen, 1990; Jahnke, 1990). The average ratios found in the sediment of this study diverges from similar ratios in other marine environments (see for instance Mach et al. (1987), Ingall and vanCappellen (1990) and deLange (1992)). However, the data are in close connection with the investigation done by Balzer (1984) in Kiel Bight in the southern Baltic proper.It seems, thus, that the fractionation and preservation of carbon and phosphorus in the Baltic Sea differ from the general pattern found in more pelagic marine environments. One probable explanation for the observed pattern may be that the settling time for organic matter in the Baltic Sea is short compared to deep sea sediments, so the fractionated decomposition has not been completed to the same degree when the organic matter finally settles on the sediment surface.

4. Summary and conclusions

Difference's in primary production, water depths, salinity and biogeochemical conditions in the bottom and pore water of the Baltic Sea results in completely different diagenetic and burial patterns of supplied organic and inorganic substances of carbon, nitrogen and phosphorus. Commonly, most of the carbon and nitrogen found in the sediments are in organic form. For carbon the main explanation is that both organic and inorganic carbonates under most circumstances are thermodynamically unstable. However, in the euxinic parts of the Baltic proper (e.g. eastern Gotland Basin), with succeeding prolonged anoxic conditions in the pore waters, it is quite common to observe autigenic precipitation of mixed manganese carbonates. Manganese is of essential importanance for such precipitation. Though a comparatively high concentration of inorganic nitrogen is reported from the Baltic Sea than from other marine areas the percentage amount at examined deposition bottoms exceeds seldom 10% of the total amount of nitrogen. However, the inorganic amount of nitrogen could not be neglected in, for instance, burial calculations and in the interpretation regarding alterations of Redfield ratios within and between different localities in the Baltic Sea.

For phosphorus, on the other hand, most of the total amounts in the sediment are inorganically bound. The main reason for that is that phosphorus during most natural conditions only exist as orthophosphate, a molecule with high reactivity to solid particles through either adsorption or precipitation. Iron adsorbs large amounts of phosphorus during oxidized conditions whereas precipitation of different kinds of phosphorus minerals are common during reduced conditions. Manganese plays an important role for the burial of phosphorus in the Bothnian Bay and in some other restricted anoxic areas of the Baltic proper. In these areas of the Baltic Sea it is common to find a high coefficient of determination between phosphorus and manganese. Ferric manganese nodule formations in the Bothnian Bay together with autigenic manganese-calcium phosphate and apatite precipitation in the Baltic proper explains most likely the high coefficient of determination between manganese and phosphorus found at these sites.

The constant vertical organic C/N ratio in the sediments of the Baltic Sea suggests most likely that the preferential release of nitrogen occur during halmyrolysis or during a very early diagenetic stage. The average C/N ratio in the southern part of the Baltic Sea is close to ten. The corresponding ratio values in the Bothnian Bay and Sea are 12. 1 and 13.1, respectively. The explanation for higher organic C/N ratios in the northern part of the Baltic Sea is most likely due to a high terrestrial organic material supply through the streams in that area of the Baltic Sea.

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Table 1. Study site description and some water and sediment characteristics. The redox potentials originate from the uppermost centimetre of the sediment. The salinity and oxygen measurements originate from the water just above (≈ 1m) the sediment surface.

Site	Position (Lat;Long)	Water depth (m)	Redox potential (mV)	Oxygen (ml/l)	Salinity (PSU)
155	56 26,57; 11 38,02	28	493	6.96	32.84
156	57 17,57; 11 28,59	75	518	5.58	34.72
157	54 44,30; 10 10,54	23	478		20.19
159	54 19,03; 11 32,57	27			
160	54 04,59; 11 10,00	22	464		17.25
166	54 59,57; 13 45,01	45	398	4.65	15.11
167	55 15,29; 15 57,56	90	396	3.65	16.53
168	55 32,53; 18 23,48	89		4.47	10.94
169	54 55,00; 19 14,44	107	36	0.71	12.26
170	55 34,59; 20 29,47	68		2.85	7.82
171	57 18,28; 20 03,33	240	-111	0.44	11.64
172	57 31,14; 23 13,14	45	-26	3.50	
174	57 28,58; 23 13,18	62		3.83	6.34
176	58 05,44; 19 59,57	183		8.14	6.31
178	58 10,59; 18 09,11	145	190	2.22	8.49
179	58 37,50; 18 31,59	215			
180	58 50,57; 20 13,03	200	-149	0.20	9.80
181	59 42,29; 24 41,12	84	61	4.25	7.[illegible]
182	59 50,30; 25 51,59	84	250	4.87	7.[illegible]
183	59 32,57; 27 46,09	35	95	6.70	6.15
184	59 45,51; 28 14,21	24	118	6.78	5.24
185	60 20,29; 28 00,29	44	10	6.88	6.23
186	59 47,21; 27 07,39	67	419	7.16	6.78
187	60 14,16; 27 15,29	61	-39	6.27	6.48
189	60 01,18; 19 32,48	214	172	7.65	6.72
190	60 59,21; 19 43,59	130	469	7.97	6.33
191	61 18,51; 20 07,31	130			
192	62 39,02; 18 59,56	200	474	6.13	5.98
193	64 18,50; 22 19,14	110	453	8.61	3.98
194	64 41,26; 22 02,57	137		8.46	3.88
195	64 54,29; 23 23,20	100	470	8.75	3.59
196	62 35,13; 19 58,28	210		6.05	6.04

Table 2. Average organic C/N and C/P ratios from the different sub-basins of the Baltic Sea. SD = standard deviation.

Basin	C/N	Low	High	SD	C/P	Low	High	SD	Counts
Baltic proper	10.0	8.0	12.6	0.89	343	115	611	88	142
Gulf of Finland	10.1	9.1	11.6	0.59	266	195	389	37	50
Gulf of Riga	10.5	9.4	11.4	0.46	266	105	684	106	90
Bothnian Sea	12.1	11.1	13.2	0.52	213	138	325	45	45
Bothnian Bay	13.1	10.3	16.3	1.3	249	108	492	102	40

Figure captions

Figure 1. Map showing the location of the sampling sites in the Baltic Sea.

Figure 2. Spatial sediment distribution (0-1 cm) of total carbon in the Baltic Sea.

Figure 3. Vertical trends of manganese and inorganic carbon in the sediments of site 171 (Gotland deep).

Figure 4. Relationship between the concentration of manganese and inorganic carbon in the sediment from site 171 (Gotland deep). The coefficient of determination (R^2) is 0.97 and the average molar ratio of 0.64 (Mn/C). The divergent values (◊) from the straight line shown in the figure originate from measurements in the uppermost 9 centimetres of the sediment profile.

Figure 5. Spatial sediment distribution (0-1 cm) of total phosphorus in the Baltic Sea.

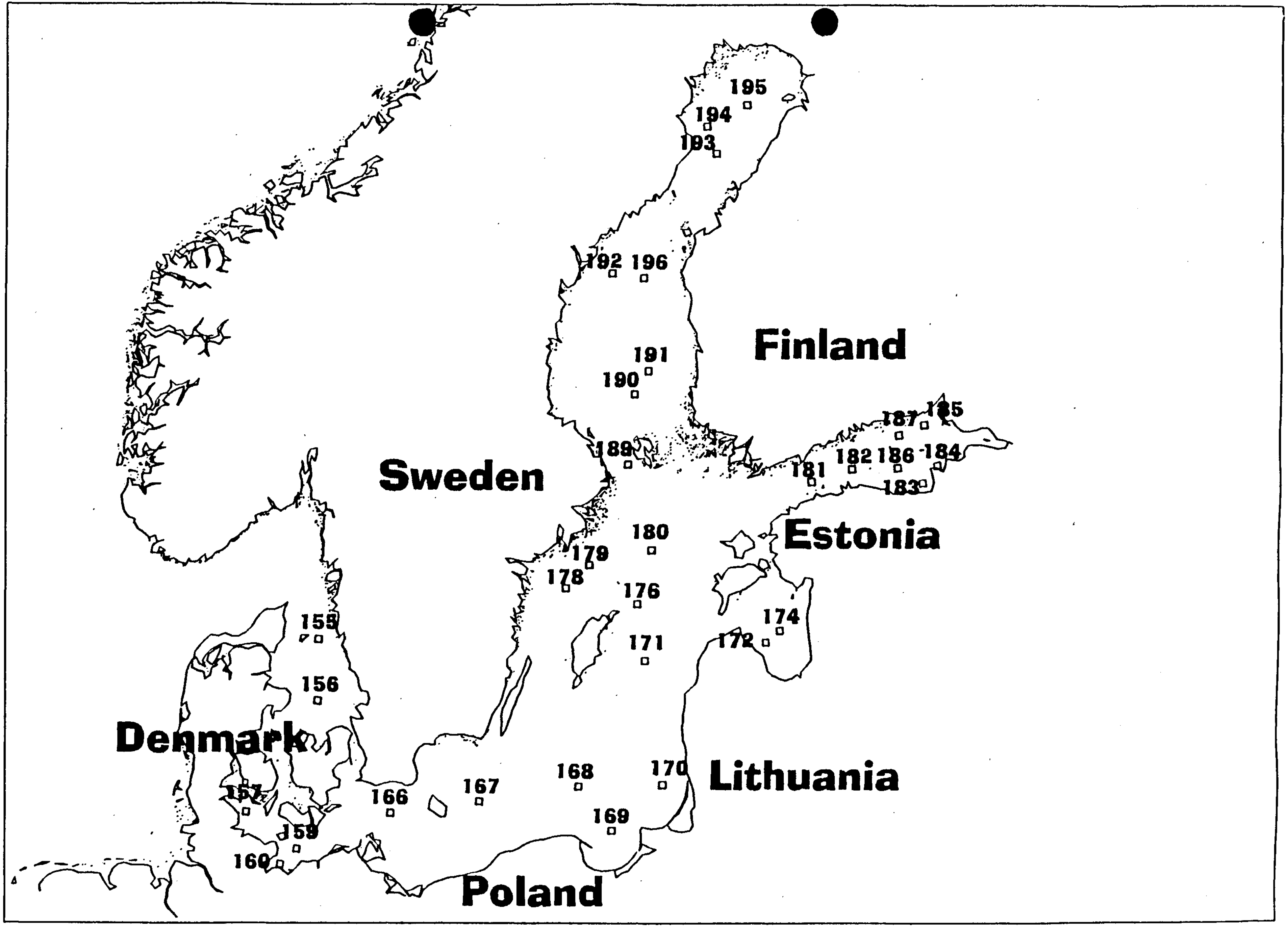
Figure 6. Vertical sediment profiles of mobile phosphorus (▲) and redox potential (○) from site 167 (Bornholm deep).

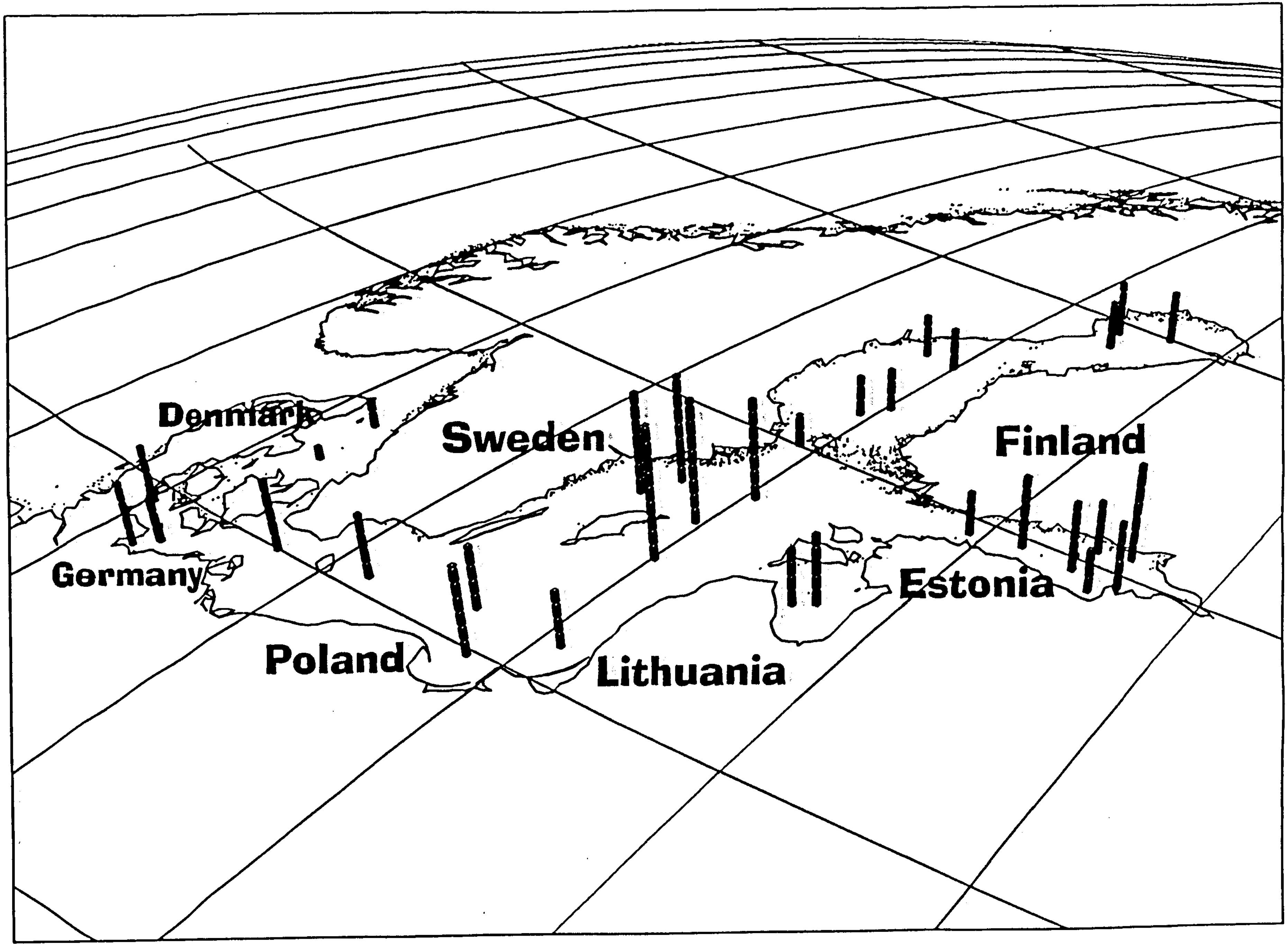
Figure 7. Vertical concentration profiles of total phosphorus (○) and manganese (▲) at site 193 and 195 (Bothnian Sea, northern Baltic Sea).

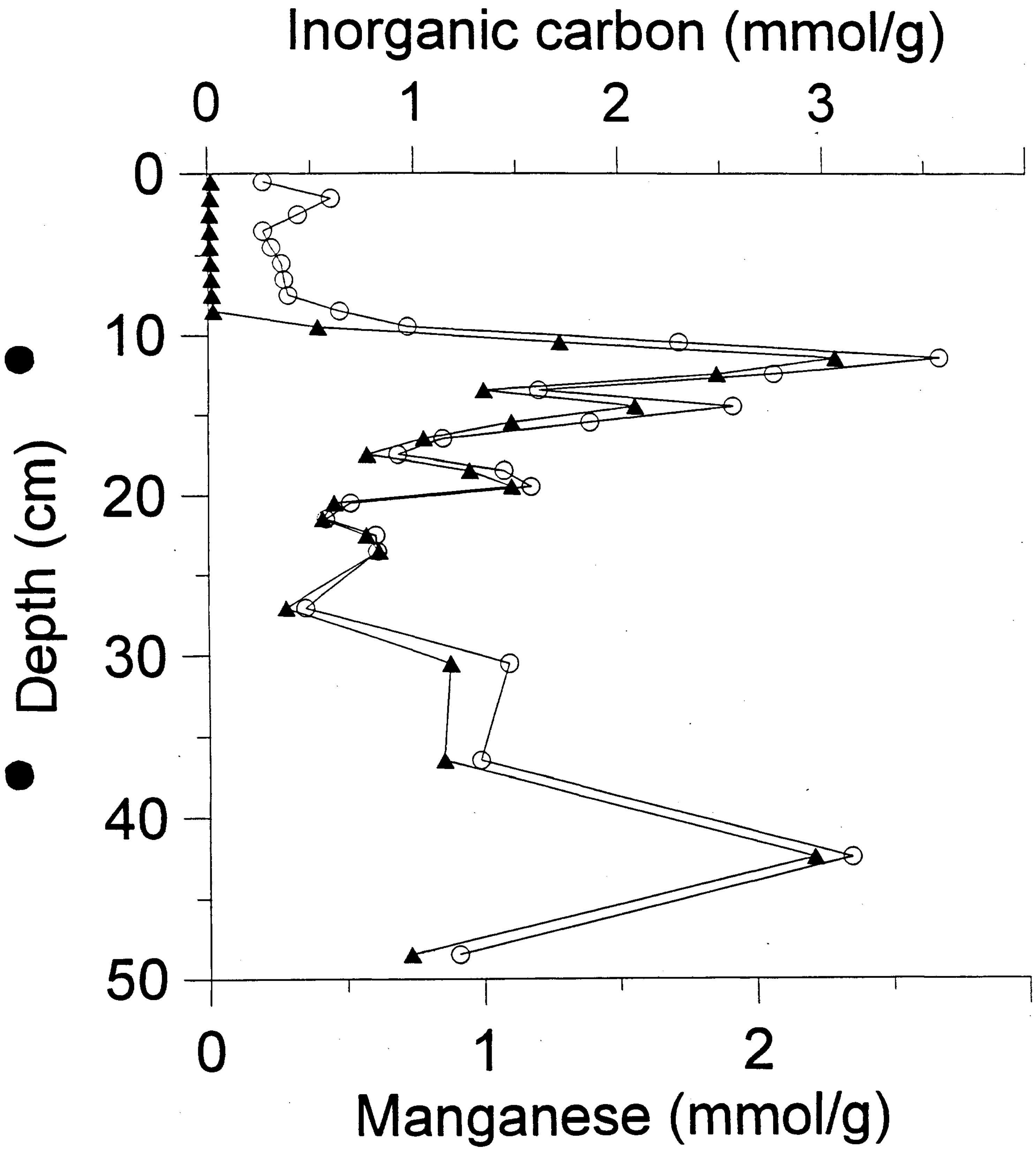
Figure 8. Relationship between the concentration of manganese (▲) and total phosphorus (○) in the sediment from sites 193 and 195.The linear coefficients of determination (R^2) from sediment sections deeper than 4 cm depth below sea floor are 0.84 and 0.86 for site 193 and 195, respectively. The average molar ratios (Mn/P) are 0.88 and 0.364 with a standard deviation of 0.17 and 0.066 for site 193 and 195, respectively.

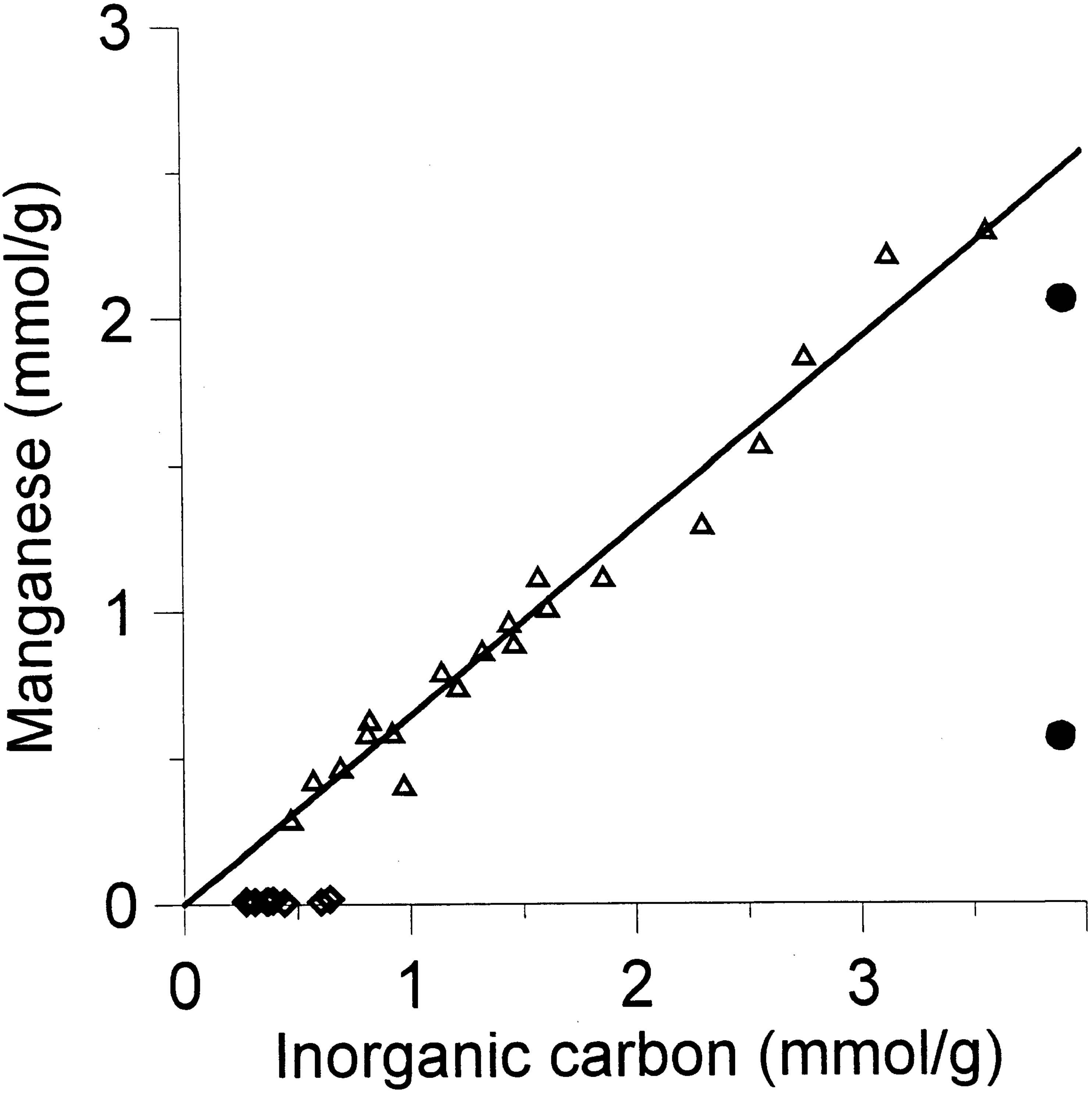
Figure 9. Relationship between the concentration of manganese (▲) and total phosphorus (○) in the sediment from sites 157 and 160.

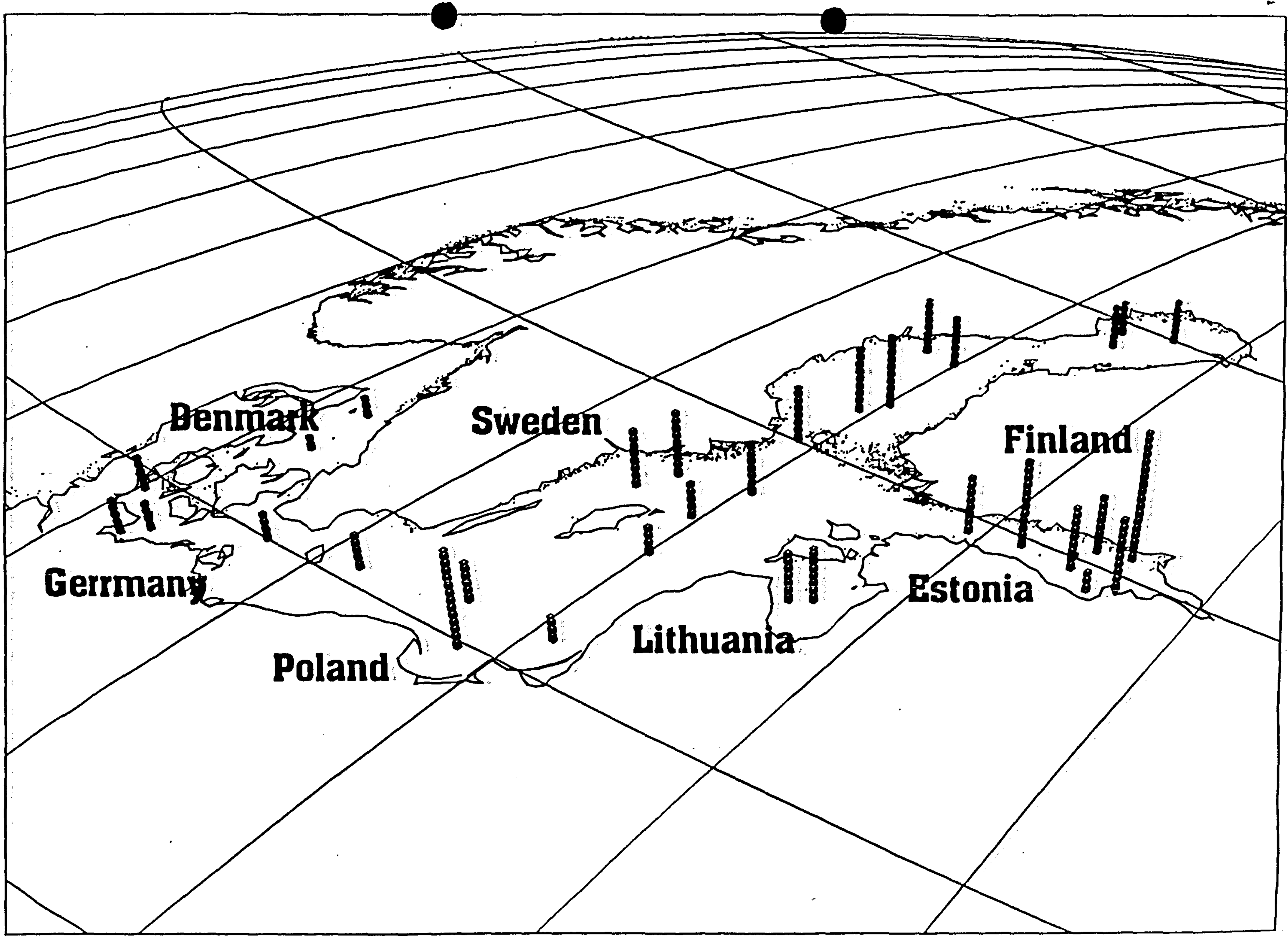
Figure 10. Sediment concentration of organic carbon versus organic nitrogen from the different sub-basins of the Baltic Sea. The linerar coefficient of determination (R^2)from the different basins is always higher than 0.9.

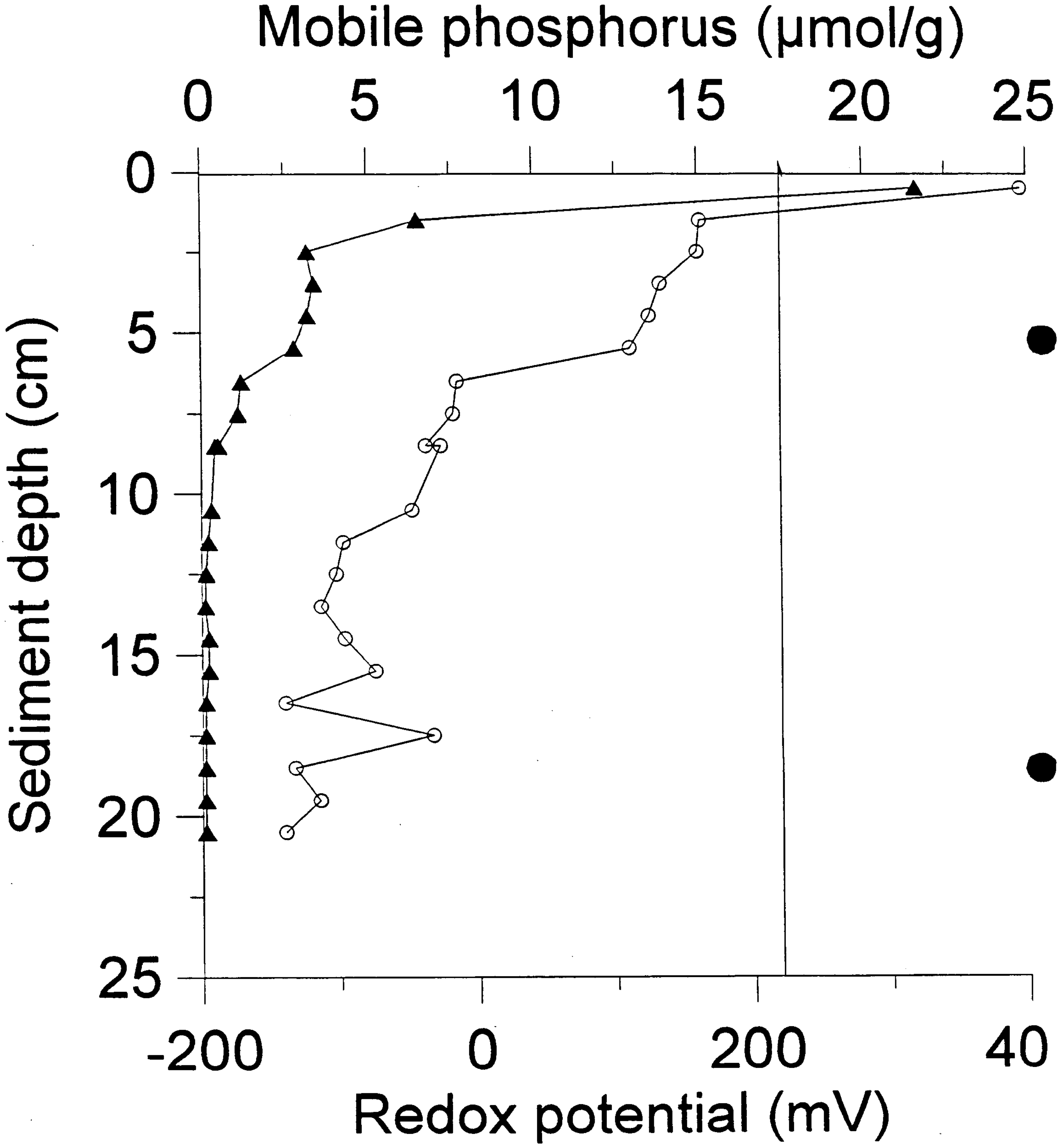

195
194
193
192
196
Finland
191
190
187
185
Sweden
189
182
186
184
181
183
180
Estonia
179
178
176
174
155
171
172
156
Denmark
170
168
Lithuania
167
166
157
169
159
160
Poland

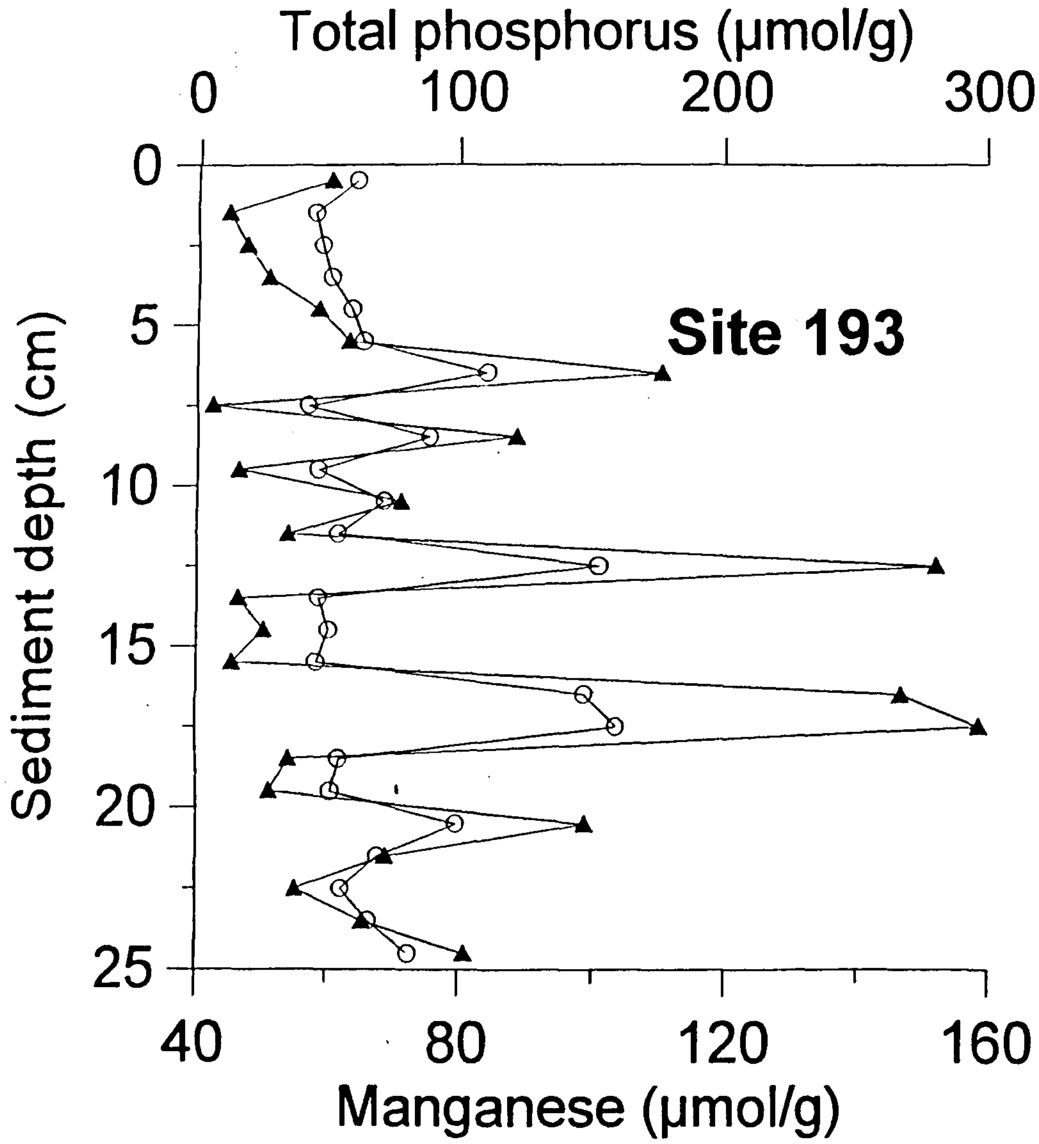

Denmark
Sweden
Finland
Germany
Estonia
Poland
Lithuania

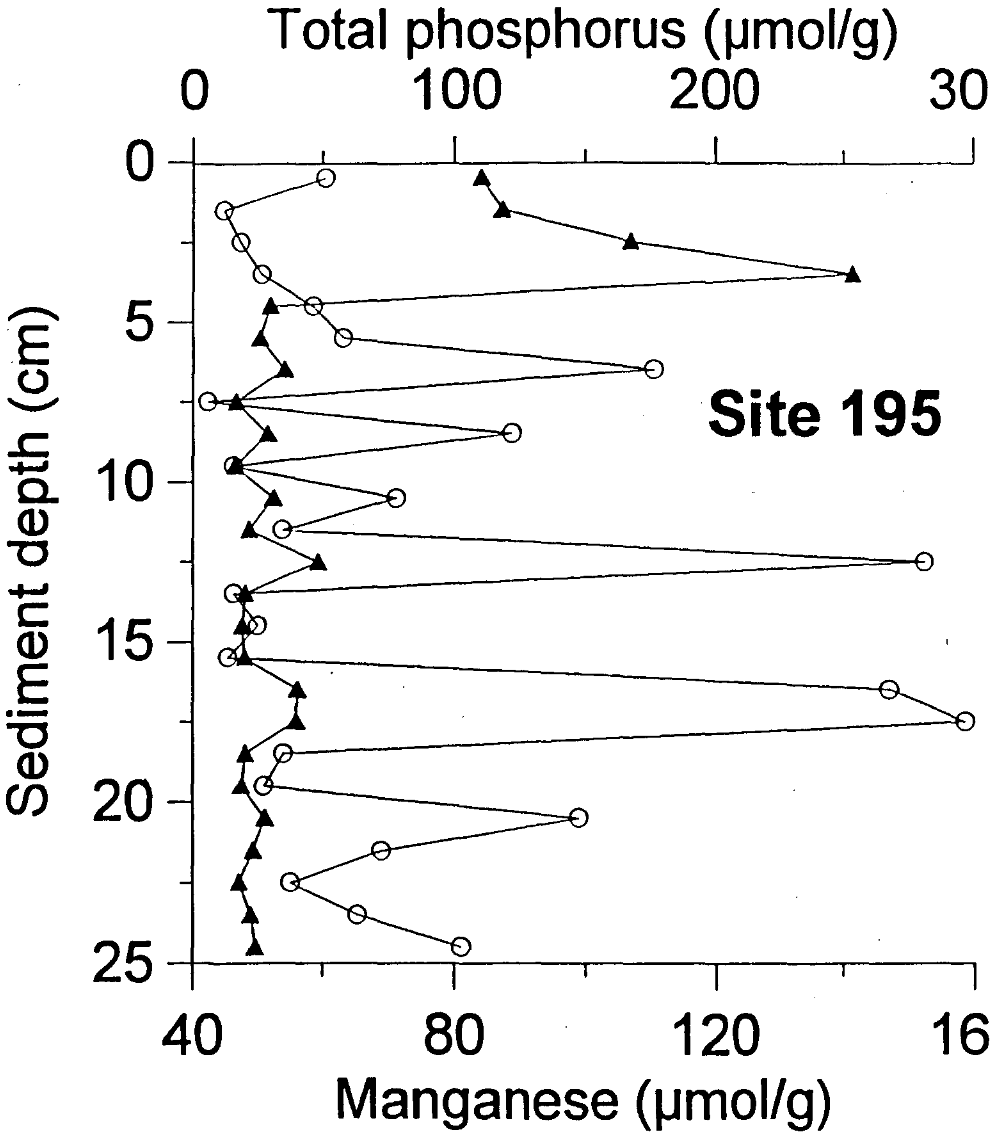

Inorganic carbon (mmol/g)
0
1
2
3
Depth (cm)
0
10
20
30
40
50
0
1
2
Manganese (mmol/g)

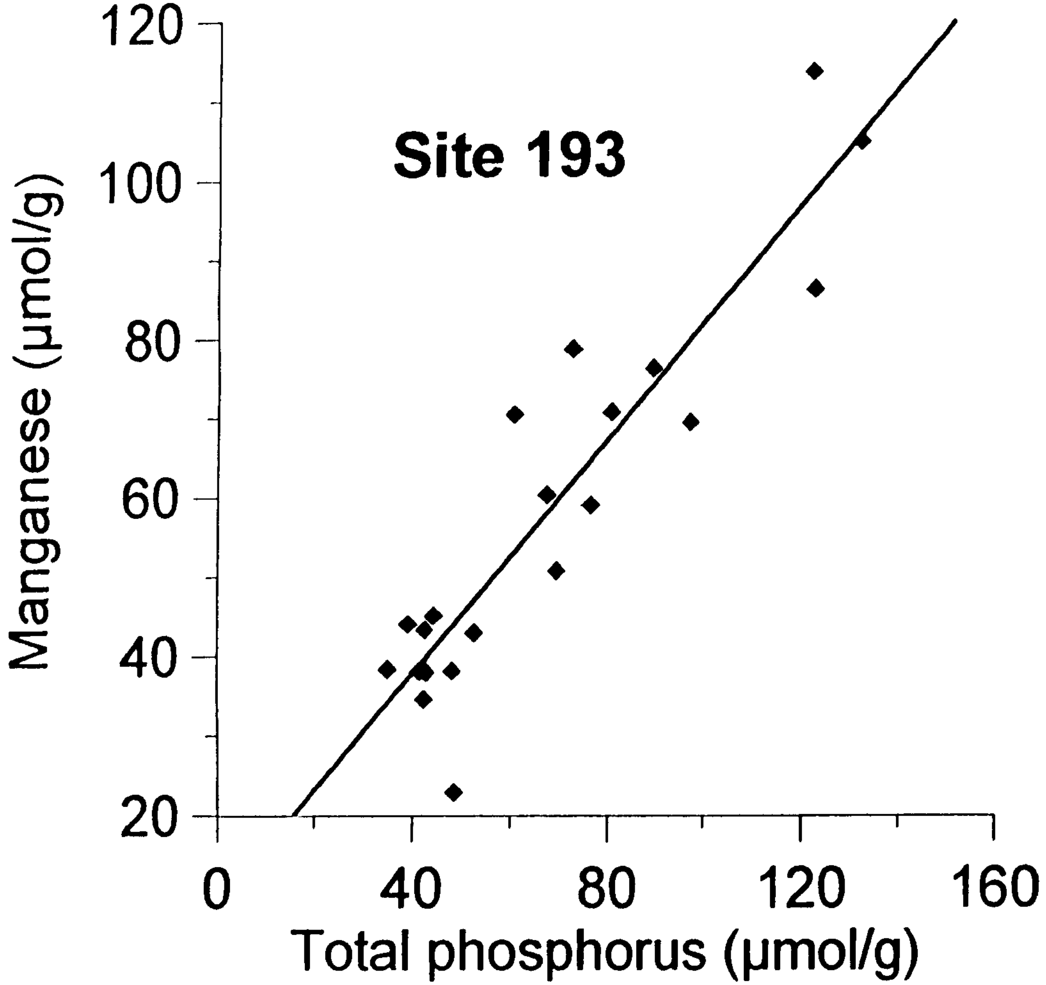

3
2
1
0
Manganese (mmol/g)
0
1
2
3
Inorganic carbon (mmol/g)

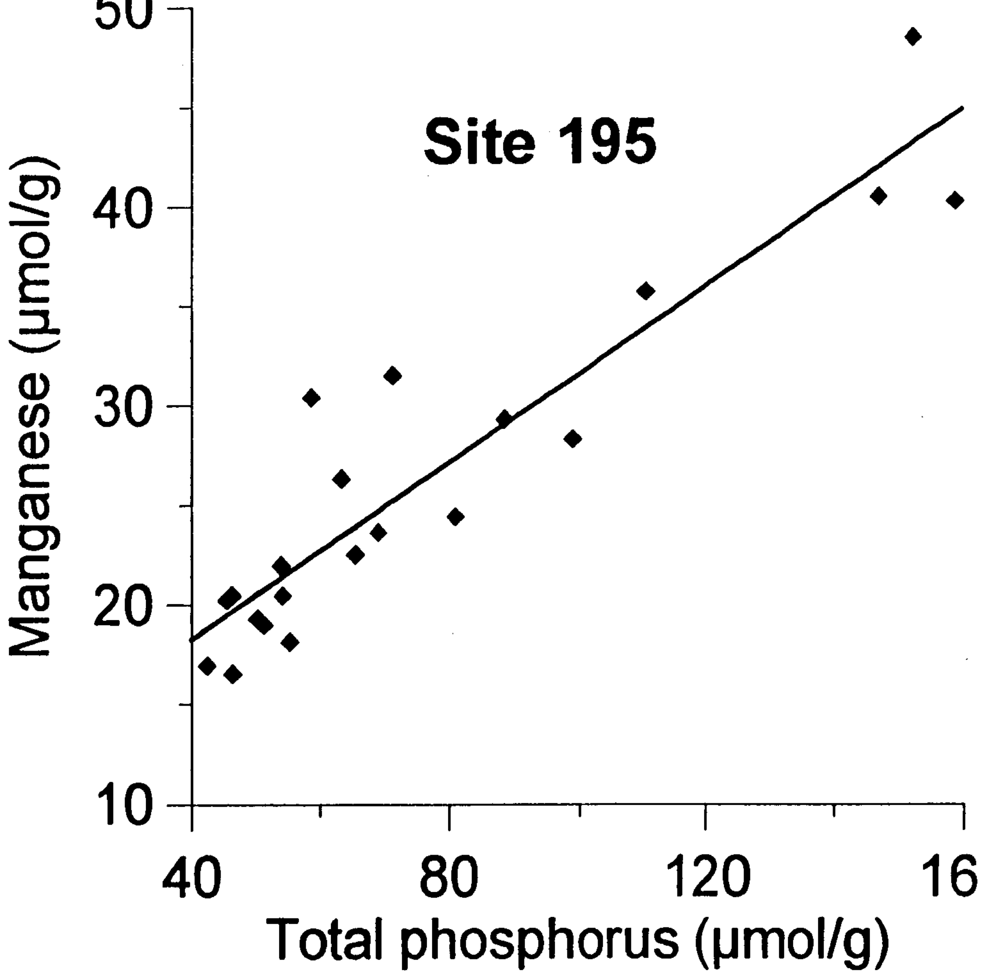

Denmark
Sweden
Finland
Gerrmany
Estonia
Lithuania
Poland

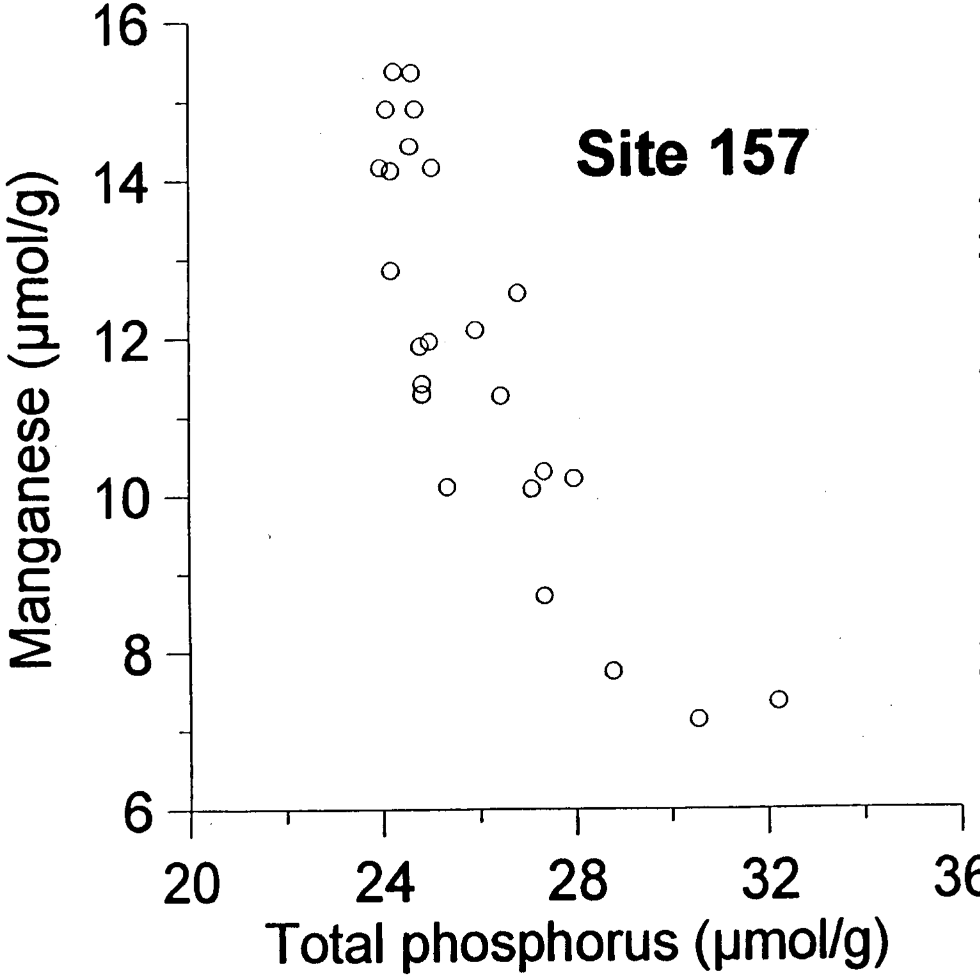

Mobile phosphorus (µmol/g)
0
5
10
15
20
25
0
5
10
15
20
25
Sediment depth (cm)
-200
0
200
40
Redox potential (mV)

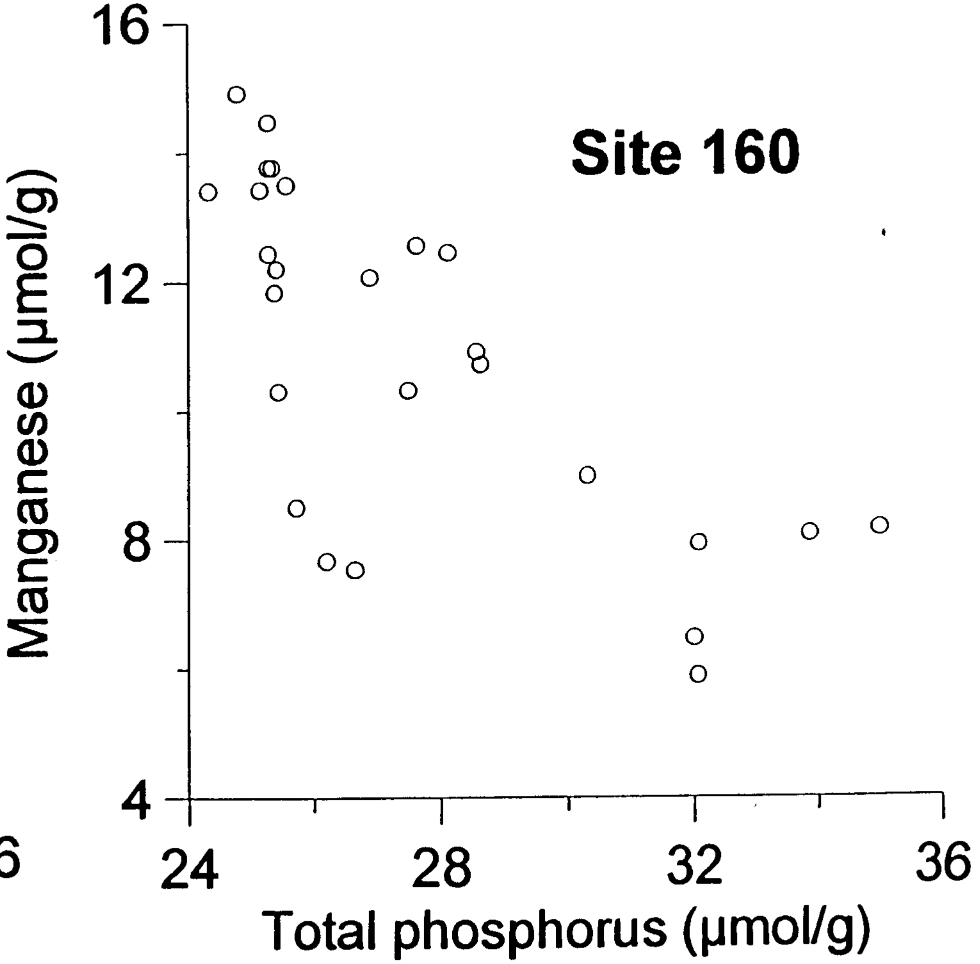

Total phosphorus (µmol/g)
0
100
200
300
Site 193
Sediment depth (cm)
0
5
10
15
20
25
40
80
120
160
Manganese (µmol/g)

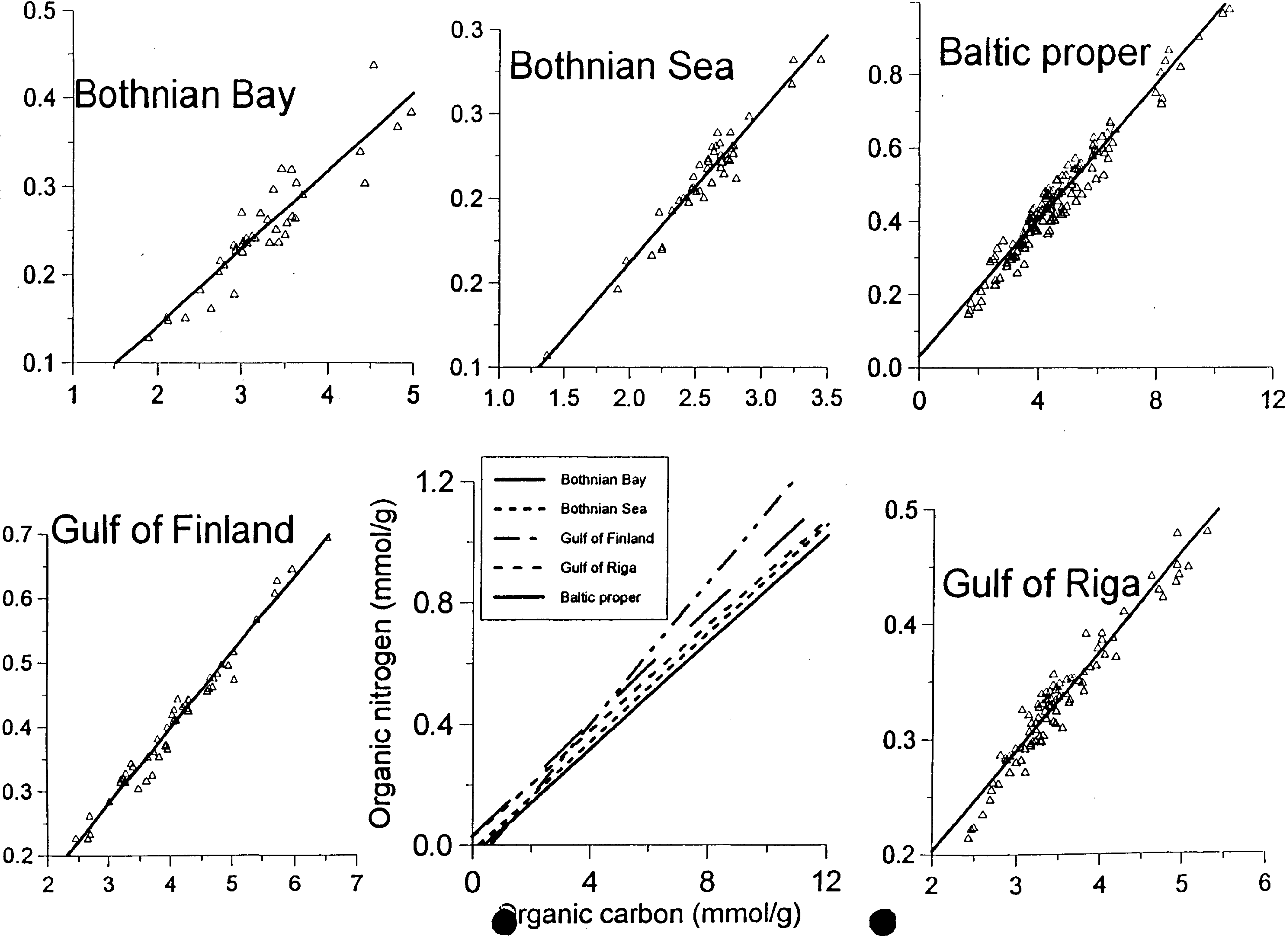

Total phosphorus (µmol/g)
0
100
200
30
Site 195
Sediment depth (cm)
0
5
10
15
20
25
40
80
120
16
Manganese (µmol/g)


Site 193
Manganese (µmol/g)
120
100
80
60
40
20
0
40
80
120
160
Total phosphorus (µmol/g)


Site 195
Manganese (µmol/g)
50
40
30
20
10
40
80
120
16
Total phosphorus (µmol/g)


Site 157
Manganese (µmol/g)
16
14
12
10
8
6
20
24
28
32
36
Total phosphorus (µmol/g)


Site 160
Manganese (µmol/g)
16
12
8
4
24
28
32
36
Total phosphorus (µmol/g)


Bothnian Bay
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
Bothnian Sea
0.3
0.3
0.2
0.2
0.1
1.0
1.5
2.0
2.5
3.0
3.5
Baltic proper
0.8
0.6
0.4
0.2
0.0
0
4
8
12
Gulf of Finland
0.7
0.6
0.5
0.4
0.3
0.2
2
3
4
5
6
7
Bothnian Bay
Bothnian Sea
Gulf of Finland
Gulf of Riga
Baltic proper
1.2
0.8
0.4
0.0
0
4
8
12
Organic nitrogen (mmol/g)
Organic carbon (mmol/g)
Gulf of Riga
0.5
0.4
0.3
0.2
2
3
4
5
6