

History of Metal Pollution and Carbon Input in Baltic Sea Sediments

Contribution Nr. 29 of the Sonderforschungsbereich 95
at the University of Kiel
„Interaction Sea — Sea Bottom“

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SUESS, ERWIN; ERLKENKEUSER, HELMUT, 1975: History of metal pollution and carbon input in Baltic Sea sediments. (Anthropogene Veränderungen der Schwermetallgehalte und der ^{14}C -Konzentration in Sedimenten der Ostsee) — Meyniana 27: 63—75, 10 fig, 3 tab., Kiel.

Concentrations of Cd, Pb, Zn, Cu, Co, Ni, Fe, and Al_2O_3 , water content, the amounts of organic carbon, the ratio of $^{13}\text{C}/^{12}\text{C}$ and the ^{14}C -activity of the organic fraction were determined with sediment depth from a 34 cm long box-core from the Bornholm Basin (Baltic Sea). The average sedimentation rate was 2.4 mm/yr. The upper portion of the core contained increasing amounts of ^{14}C -inactive organic carbon, and above 3 cm depth, man-made ^{14}C from atomic bomb tests. The concentrations of the heavy metals Cd, Pb, Zn, and Cu increase strongly towards the surface, while other metals, as Fe, Ni and Co remain almost unchanged. This phenomenon is attributed to anthropogenic influences. A comparison of the Kieler Bucht, the Bornholm and the Gotland Basins shows that today the anthropogenic addition of Zn is about 100 mg/m² · yr in all three basins. The beginning of this excess of Zn, however, is delayed by about 20 years in the Bornholm Basin and by about 40 years in the Gotland Basin. It is suggested that SW-NE transport of these anthropogenically mobilized metals may be related to periodic bottom water renewal in the Baltic Sea sedimentary basins.

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Kurzfassung

An einem 34 cm langen Sedimentkern aus dem Bornholm Becken wurden die Konzentrationen von Cd, Pb, Zn, Cu, Co, Ni, Fe und Al_2O_3 , der Wassergehalt, der Anteil von organischem Kohlenstoff, sowie das $^{13}\text{C}/^{12}\text{C}$ -Verhältnis und die ^{14}C -Aktivität der organischen Fraktion in Abhängigkeit von der Tiefe untersucht. Die mittlere Sedimentationsrate beträgt 2.4 mm/Jahr. Der obere Kernabschnitt enthält in zunehmendem Maße ^{14}C -inaktiven organischen Kohlenstoff und, oberhalb von 3 cm Sedimenttiefe, künstliches ^{14}C aus den Atomwaffenversuchen. Zugleich nimmt die Konzentration der Schwermetalle Cd, Zn, Pb und Cu zur Oberfläche hin stark zu, während andere Metalle wie Fe, Ni und Co nahezu unverändert bleiben. Dieser Befund wird auf anthropogene Einflüsse zurückgeführt. Ein Vergleich zwischen Kieler Bucht, Bornholm Becken und Gotland Becken zeigt, daß die anthropogene Zufuhr von Zink in allen drei Sedimentationsbecken heute gleichermaßen etwa 100 mg/m² · J. beträgt. Doch beginnt die erhöhte Zn-Zufuhr im Bornholm Becken etwa 20 Jahre, im Gotland Becken etwa 40 Jahre später als in der Kieler Bucht. Es wird die Möglichkeit eines SW-NO-wärts gerichteten Transportes in Verbindung mit dem Einstrom salzreicheren Bodenwassers aus der Beltsee diskutiert.

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1. Introduction

A characteristic assemblage of heavy metals cadmium, lead, zinc, and copper, and of inactive (= old) organic carbon in excess to the radiocarbon isotope concentration in near surface sediments of the western Baltic Sea (Kieler Bucht) have been suggested as documenting the age of industrialization in the sedimentary record (ERLENKEUSER et al., 1974). The history of lead pollution as reflected in the isotopic composition has also been recorded in sediments from the Southern California coastal zone (CHOW et al., 1973). In river and lake deposits (FÖRSTNER und MÜLLER, 1974), in annual layers of the Greenland and Antarctic ice sheets (MUROZUMI et al., 1969), and in various other terrestrial sites dramatic increases in certain metal concentration have been related to anthropogenic sources (TYLER, 1972). The rates of anthropogenic mobilization of cadmium, lead, zinc, and copper are many times higher than what natural fluxes would supply to the various sedimentary environments. For the western Baltic Sea these fluxes have been estimated at 120 mg/m²·yr. Similar rates of anthropogenic fluxes of heavy metals to the sediments were found in the California coastal basins (BRULAND et al., 1974) and it is attempted with the investigations reported here to extend such estimates to other areas of the Baltic Sea in order to gain a more quantitative insight into long-term anthropogenic effects on the natural environment and to obtain information on their extent and spreading.

At the present time little is known about the mechanisms and distances of transport, of metals pollutants whether they are predominantly carried in aerosols, particulates or in the dissolved state, nor about the chemical state and speciation in which they are transported and deposited or their geochemical behavior after deposition. Therefore, it is difficult to properly evaluate the evidence for increased metal deposition collected so far because removal of metals (in most cases potentially toxic metals) from the atmosphere and hydrosphere and their fixation in the sedimentary environment might represent a less disadvantageous process than their remaining in the biological and hydrological cycle. Some of the above aspects will be considered along with the results obtained from the sediments of three Baltic Sea sedimentary basins.

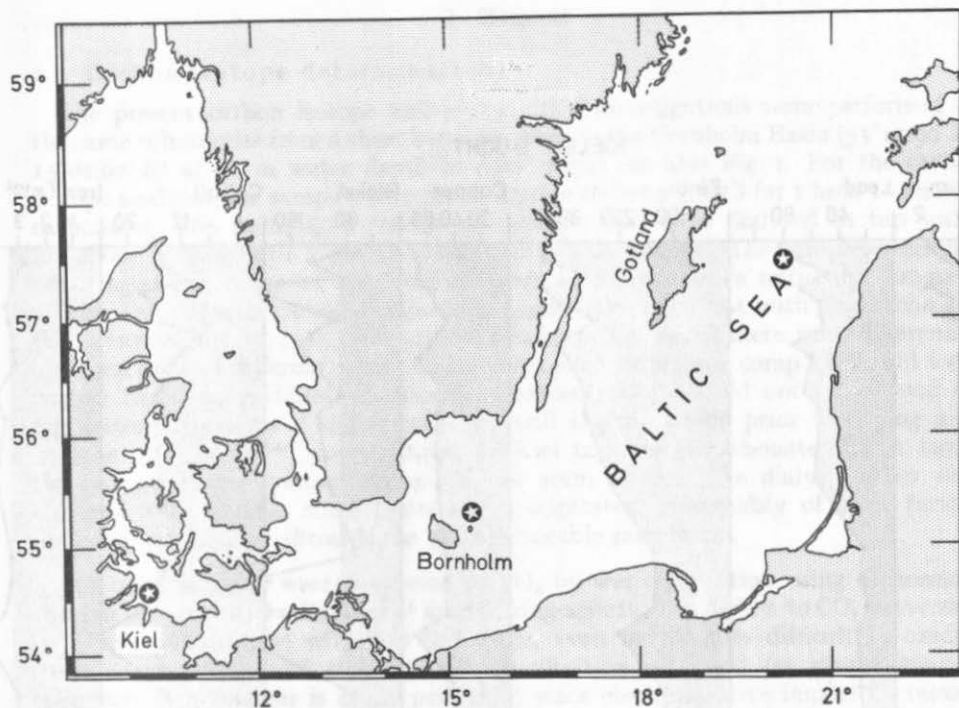


Fig. 1: Sample locations at the western and central Baltic Sea: Kieler Bucht, Bornholm Basin, and Gotland Basin.

Entnahmepunkte der Sedimentkerne: Kieler Bucht, Bornholm Becken und Gotland Tief.

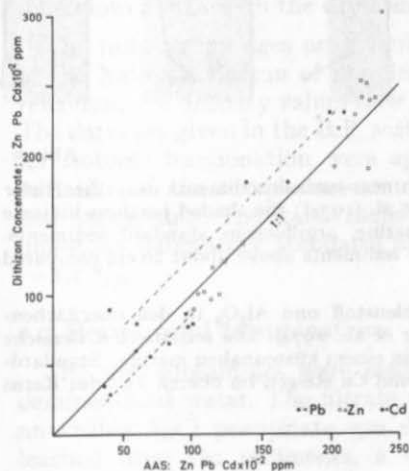


Fig. 2:

Metal determination by atomic absorption spectroscopy directly from hydrofluoric/perchloric acid-digested sediment solutions (AAS) and after pre-concentration by dithizon extraction (DITHIZON). Background effects with direct AAS determinations are thought to cause the positive and negative deviations respectively, in comparison to the dithizon extract for Cd and Pb.

Vergleich der Schwermetallbestimmungen durch die Atomabsorptionsmethode bei unterschiedlicher Probenbehandlung: (AAS): Analyse direkt aus Probenauflösung durch Flußsäure und Perchlorsäure. (DITHIZON): Analyse nach Probenauflösung und Voranreicherung durch Dithizon-Extraktion. Abweichungen von der Soll-Geraden sind wahrscheinlich durch systematische Variationen des Untergrundes bei der erst genannten Methode (AAS) bedingt.

Abb. 2:

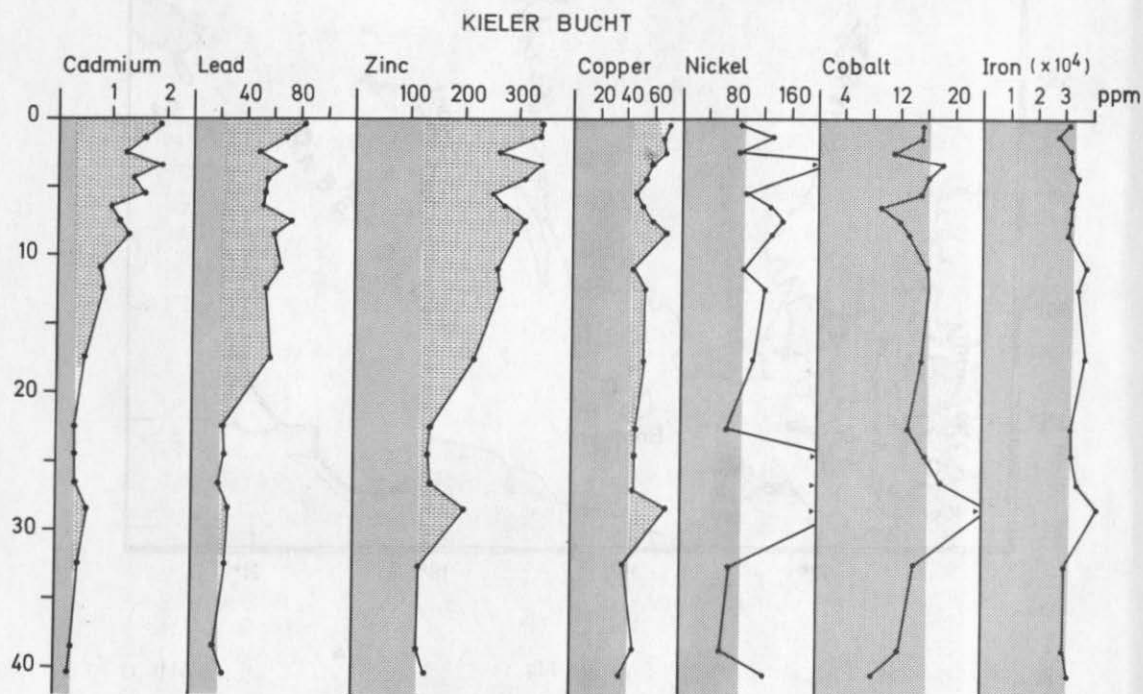


Fig. 3:

Heavy metal, organic carbon, and alumina contents in near-surface sediments from the Kieler Bucht (Western Baltic Sea) according to Erlenkeuser et al. (1974); the shaded portions indicate the respective metal concentrations of nearshore, marine, argillaceous standard sediments. Cd, Pb, Zn, and Cu exhibit a pronounced excess in the sediments above about 20 cm compared to the deeper portions of the core.

Abb. 3:

Konzentration von Schwermetallen, organischem Kohlenstoff und Al_2O_3 in den oberflächennahen Sedimenten der Kieler Bucht (nach Erlenkeuser et al., 1974). Die schattierten Bereiche kennzeichnen die Konzentration des jeweiligen Metalls in einem küstennahen marinen Standard-Tonsediment. Die Konzentrationen von Cd, Pb, Zn und Cu steigen im oberen Teil des Kerns zur Oberfläche hin stark an.

2. Methods

2.1. Carbon isotope determinations

The present carbon isotope and heavy-metal investigations were performed on the same subsamples from a short box core taken in the Bornholm Basin ($55^{\circ}17.90' N$; $15^{\circ}02.00' E$) at 71 m water depth in April 1974; see also Fig. 1. For the carbon isotope analyses, the samples were pre-treated with hot 2% HCl for 1 hour to remove carbonates. The particulate residue and excess acid were dialysed in tap water for about 6 days until a pH of about 5 to 6 was reached. The samples were not centrifuged nor decanted and washed prior to dialysis since noticeable amounts of dissolved organic carbon compounds might have been lost with this technique (ERLENKEUSER *et al.*, 1975), affecting the radiocarbon age if there were differently-aged fractions of different solubilities present such as organic compounds and fossil carbon from fuel residues. Radiocarbon concentration should not be affected by tap water carbonates if the samples are still slightly acidic prior to drying and, because of the low ^{14}C concentration of Kiel tapwater bicarbonate (ENGE, 1971), the risk of sample contamination did not seem serious. The dialysis tubes were changed after 3 days since hydroxide precipitates, presumably of iron, further impede ion exchange through the semi-permeable membrane.

The dried samples were converted to CO_2 by wet combustion using dichromate and hot concentrated sulfuric acid as oxidizing agents. The carbon to CO_2 conversion is always quantitative with this technique, even for samples difficult to oxidize (such as graphite), and the final CO_2 purification necessary for proper counter operation with this gas is easily performed since electronegative impurities remain much lower than with the dry combustion method.

The radiocarbon ages are calculated with a ^{14}C half-life of 5568 yrs., and 95 % of the National Bureau of Standards oxalic-acid ^{14}C standard activity is used for reference. ^{14}C activity values refer to this activity and are here expressed as % STD. The dates are given in the B.P. scale with A.D. 1950 as reference year. No corrections for isotopic fractionation were applied. The errors given correspond to the 1σ variation of the sample net-counting rate which includes statistics for standard and background. The stable carbon-isotope ratios were measured against Solnhofen limestone (laboratory standard) and were converted to the PDB scale by adding -1.1‰ .

2.2 Heavy metal determinations

The wet subsamples were desalted by repeatedly suspending and filtering in demineralized water. The filtrate was checked with acidified $AgNO_3$ solution until no visible $AgCl$ precipitate was detected. In addition to the seawater salts thus leached from the sediments, a considerable amount of phosphate, silica, iron, manganese, and some organic components (= humic or yellow substances) were removed by this treatment, but no Zn, Pb, nor Cu could be detected in the wash water. The sediments were subsequently dried under vacuum at about $30^{\circ}C$ and then ground for further analyses.

About one gram of each dried sediment sample was digested by standard perchloric/hydrofluoric acid treatment, dissolved in hot 6 n HCl and diluted to 50 ml with demineralized/deionized water. Since interference with atomic absorption spectrometric (AAS) determination of the trace metals by large concentrations of iron, manganese, alumina, calcium and sodium was suspected, the metals were pre-

concentrated in a dithizon extract, then digested in perchloric acid and measured by AAS. In addition, Zn, Pb, and Cd were also determined directly from the digested sediment solution in a number of samples in order to evaluate the results of the more laborious pre-concentration technique. The reagents and procedure according to Koch and Koch-Dedice (1974) were slightly modified and are here described in detail; the results were compared to the determinations obtained directly from the digested sediment solutions.

2.2.1 Dithizon purification

Commercial dithizon (1 g/500 ml) was dissolved in chloroform and extracted with 1% aqueous NH_3 -solution four times in order to remove the oxidized portion which remains in the chloroform phase. The aqueous phase was then acidified with HCl to a pH of 1-2 and the re-precipitated dithizon was back-extracted with chloroform. The chloroform phase was washed again with weakly acidified H_2O ; the purified concentrated dithizon solution was stored in a brown bottle under diluted sulfuric acid.

2.2.2 Extraction

About 40 ml of digested sediment solution were filtered to remove barium sulfate precipitates which formed occasionally; dissolved iron and manganese were masked with two portions of 20% K-Na-tartrate solution prior to extraction of the trace metals. Between adding this complexing agent the sample solution was brought to approximately pH 8.5 with concentrated NaOH, and after adding the second portion of Na-K-tartrate solution (5 ml) the pH was finally adjusted to 8.5 ± 0.05 . After transferring the sample solution to a 250-ml separatory funnel and adding 50 ml of the diluted dithizon concentrate (1:10), the sample was vigorously agitated by a mechanical shaker. Upon separation the chloroform phase was collected and the extraction procedure repeated with dithizon concentrate diluted 1:100 until the extract showed no detectable color change. Then the pH was changed by 0.5 units and the extraction was repeated; with this step-by-step procedure the required pH-range of 8.5 to 10.5 was covered and all resulting extracts were combined.

2.2.3 Digestion

After evaporating off the chloroform, the dithizon-metal residue was refluxed with 5 ml of 60% perchloric acid for 6 hours and then completely dried. The remaining perchlorates were dissolved in 1 ml of 6 N HCl and diluted to 5.00 ml. The metals were subsequently determined by atomic absorption spectroscopy, calibrated with standard solutions.

Figure 2 shows the results of direct metal determinations (AAS) and after pre-concentration (DITHIZON). It is clear that the pre-concentrated Pb determinations are significantly lower than the direct (AAS) values, that Cd shows the opposite, whereas the Zn values are not significantly different. The slopes of the respective regression lines are close to 1; it appears that in the case of Pb, either incomplete dithizon extraction or a higher-than-expected background absorption contributed to the high AAS values. The second possibility is more likely since absorption of a NaCl-matrix solution is higher at the wave length for Pb than at other wave lengths.

3. Baltic Sea sedimentary basins

A series of basins of increasing depths are located roughly along the W—E axis of the Baltic Sea. In two of them, the Gotland Basin with a maximum depth of 249 m and the Bornholm Basin with a maximum depth of 90 m, anoxic conditions develop in the bottom water layers for shorter or longer periods of time depending upon the frequency and intensity of well-oxygenated North Sea water inflows (FONSELIUS, 1962; 1969; WYRTKI, 1954). The Kieler Bucht is part of the Western Baltic Sea or Belt Sea, the first and shallowest (30 m) of the series of basins (SEIBOLD et al., 1971; MAGAARD and RHEINHEIMER, 1974). When periods of inflows develop under certain weather conditions, the saltier North Sea water penetrates through the Danish Belts and fills first the deeper parts of the Western Baltic Sea until a first sill at 30 m permits overflow into the Arkona Basin. From there a second sill determines the further flow into the Bornholm Basin and another sill at ~60 m, the flow into the Gotland Basin. The main source for present day sediments are reworked glacial till deposits in and around the Baltic Sea. Their distribution and thicknesses are determined by the bottom morphology and hydrographic conditions (LARSEN and KÖGLER, 1975; WINN, 1974; GRIPENBERG, 1934; and others). In the deep basins the fine-grained, carbonate-free clay mineral fraction is generally re-deposited with varying proportions of quartz silt and authigenic fractions, i.e., metal sulfides, phosphates, secondary carbonates, and a significant percentage of organic matter of around 5 wt.% of organic carbon. Due to the anoxic environment above the sediment water interface, or at least due to the strongly reducing conditions that develop a few millimeters to one centimeter below the sediment surface, benthic organisms are rare. Consequently, bioturbation is not well developed and primary sedimentary structures are preserved in laminations and well-developed bedding features as can be observed in radiographs (WINN, 1974). The sedimentation rate in the basins of the Baltic Sea is generally about one to three millimeters per year. Where stronger bottom currents prevail, such as in the northern entrance of the Great Belt channel, reduced sedimentation is observed (WINN, 1974; ERLÉNKEUSER et al., 1975), and occasional events of erosions may entirely reduce large parts of the postglacial marine sediment sequence, as was observed in the Breitgrund Channel, Western Kieler Bucht. The particulate matter may be preferably transported to and deposited in the lower energy environment at the channel outlets.

Low post-depositional disturbance and high authigenic organic carbon content favor dating of the sediment by the ^{14}C -method. The ^{14}C -level of authigenic organic matter in the Baltic Sea is the same as, or slightly less than, that of the atmosphere, if isotopic fractionation effects are taken into account. The carbon dioxide exchange with the atmosphere is rapid enough (ERLÉNKEUSER et al., 1975) to cancel out any different ^{14}C -levels which the various fresh water discharges into the Baltic Sea might have. Wave action and bottom currents, however, rework old organic matter, which is redeposited along with the authigenic carbon, and the final radiocarbon age of the total organic matter is roughly 1000 yrs. older than the depositional age. The magnitude of this age shift probably depends on the sedimentary environment. This environment seems to have been rather constant (± 150 yrs.) for Kieler Bucht sediments during the last millenium (ERLÉNKEUSER et al., 1974). At least in part, these small scale ^{14}C variations are correlated with the total organic carbon content and might be quantitatively understood as varying amounts of authigenic organic carbon in the sediments.

4. Results

4.1 Heavy metal distribution

Earlier investigations, restricted to sediments of the Kieler Bucht, yielded a characteristic heavy metal assemblage in near-surface sediments; i.e. cadmium, lead, zinc, and copper were increasingly concentrated in younger deposits (ERLENKEUSER et al., 1974). These results are reproduced in Fig. 3 for one of two sediment cores from the Kieler Bucht. The shaded portions of the concentration - vs. - depth diagrams represent standard background values of the respective metals for near-shore, marine, argillaceous deposits (TUREKIAN and WEDEPOHL, 1961). A measurable deviation from this background showed increasingly higher metal contents at about 22 cm of sediment depth, disregarding one sample at 28 cm which appeared to contain additional metals in the form of heavy minerals. New results obtained from a carefully sampled depth-profile of a box-core from the central part of the Bornholm Basin yielded a similar heavy metal distribution (Fig. 4). Again cadmium, lead, zinc, and copper were significantly enriched in the younger, uppermost sediment layers, whereas nickel, cobalt, and iron, although fluctuating, showed no systematic concentration changes. The shaded portions of these diagrams again represent background values. It should be pointed out, that here the background values are not those of the "standard near-shore, marine, argillaceous sediment" as in Fig. 3, but are extrapolated values from those concentrations measured in the deeper portions of the core. The high backgrounds of cadmium and lead in the Bornholm Basin sediments, as compared to those in the Kieler Bucht, are probably due to the higher clay content and the associated organic matter, seen in the higher Al_2O_3 and organic carbon concentrations listed in Table I. The zinc and copper background values are approximately the same in all these sedimentary basins, whereas nickel and cobalt appear to be much higher in the Kieler Bucht sediments. This could conceivably be due to high cobalt contents in the reagents used and to background problems, but the abnormally high nickel content still needs an explanation. Variations in iron parallel those of alumina and organic carbon concentrations between the two sites. Taking these variations and isotopic evidence as presented below into account, it is clear that the first deviation from the natural background for cadmium, lead, zinc, and copper can be placed at a depth of around 16 cm, and a further, more pronounced deviation can be located between the surface and 10 cm of sediment depth.

The zinc and copper contents between the surface and 30 cm of depth in sediments of the Gotland Basin are shown in Fig. 5. These data are from HALLBERG (1974) who has analysed sections of 2 mm thickness from a continuous core of about 45 cm in length. Each of the values plotted on the concentration - vs. - depth diagrams in Fig. 4 represents the average of five 2-mm sections from one-centimeter core intervals as reported by HALLBERG. The "standard" zinc and copper background values are also shown by the shaded areas, and it is obvious that in the Gotland Basin, too, zinc and to a lesser degree copper contents are larger than the background values in the near surface sediments. Here, however, the deviations first begin at a rather shallow depth of about 6 cm. Molybdenum, organic carbon, and nitrogen determinations are also available from these sediments, but unfortunately no cadmium, lead, cobalt, nickel, or iron analyses were performed, so complete comparison of the Gotland Basin sediments and the Bornholm Basin and the Kieler Bucht sediments is not possible. Since the zinc-deviation is so well documented in the Gotland Basin sediments and also because the zinc determinations can be performed

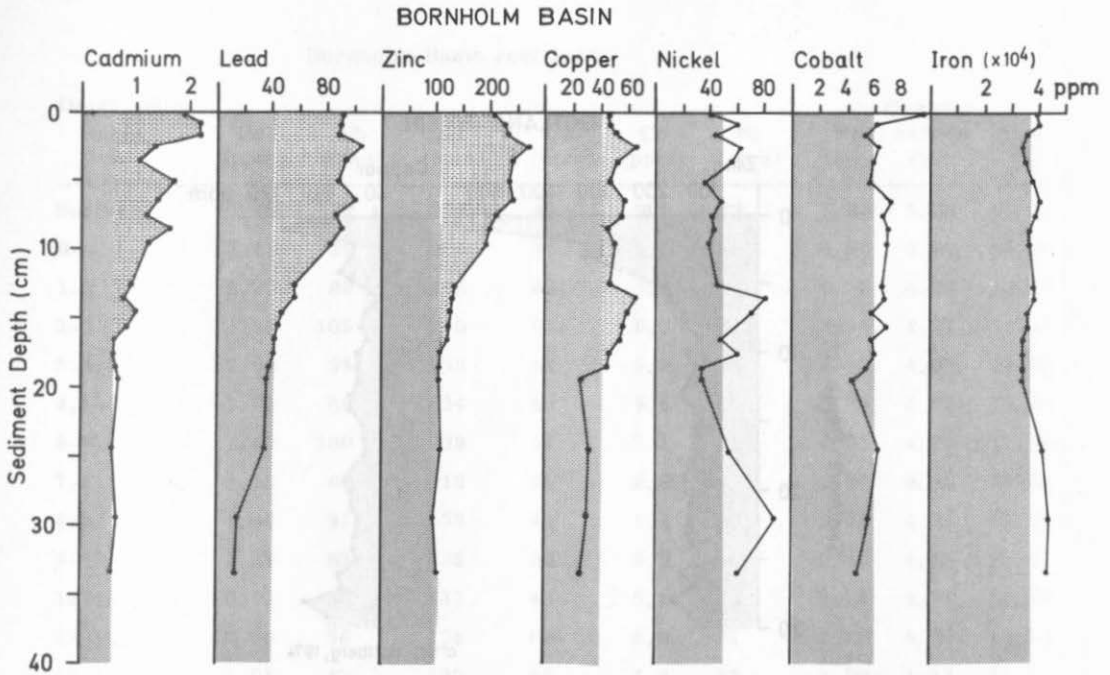


Fig. 4:

Heavy metal, organic carbon, and alumina contents in near-surface sediments from the Bornholm Basin; here a pronounced increase in Cd, Pb, Zn, and Cu is noticeable between the surface and 16 cm of sediment depth.

Abb. 4:

Konzentration von Schwermetallen, organischem Kohlenstoff und Al_2O_3 in den oberflächennahen Sedimenten des Bornholm Beckens. Oberhalb von 16 cm Sedimenttiefe nehmen die Cd-, Pb-, Zn- und Cu-Konzentrationen stark zu.

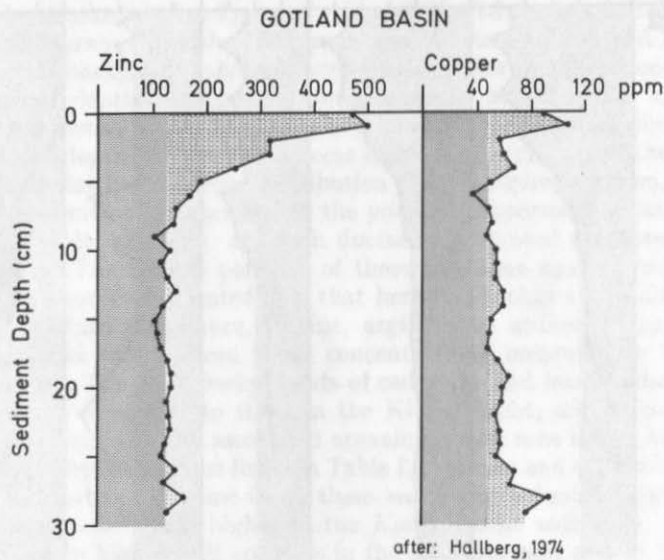


Fig. 5:

Zinc and copper contents in near-surface sediments from the Gotland Basin; the pronounced increase in metals is restricted to the upper 6 cm of the core. Data are from Hallberg (1974).

Abb. 5:

Zn- und Cu-Konzentration in den oberflächennahen Sedimenten des Gotland Beckens. Die höheren Konzentrationen dieser Elemente beschränken sich auf den Tiefenbereich bis 6 cm.

Bornholm Basin sediments

Depth below surface (cm)	Cd (ppm)	Pb (ppm)	Zn (ppm)	Cu (ppm)	Co (ppm)	Ni (ppm)	Fe (%)	Organic carbon (%)	Al ₂ O ₃ (%)
Surface	1.88	92	204	45	9.5	39	3.95	5.09	13.52
0-1	2.19	90	224	46	6.1	60	4.00	5.09	13.55
1-2	2.20	88	232	49	5.3	43	3.56	4.96	13.42
2-3	1.32	105	270	65	6.3	62	3.38	4.97	13.07
3-4,5	1.06	93	238	52	5.9	56	3.47	4.98	13.90
4,5-6	1.73	88	234	46	5.6	36	3.74	5.00	15.50
6-7	1.40	100	239	57	7.1	48	4.03	4.72	12.50
7-8	1.19	86	213	55	6.6	42	3.88	4.58	13.80
8-9	1.66	91	198	44	7.0	43	3.65	4.35	14.36
9-10	1.22	83	192	50	6.9	39	3.65	4.45	13.07
12-13	0.93	56	137	46	6.5	46	3.86	4.77	11.27
13-14	0.80	56	136	65	6.8	81	3.85	4.10	11.60
14-15	1.01	47	128	58	5.8	70	3.60	4.12	11.30
15-16	0.83	44	124	46	7.0 (186)		3.61	4.28	11.57
16-17	0.62	42	118	44	5.8	49	3.47	4.13	11.14
17-18	0.59	41	107	36	6.0	61	3.48	4.12	11.10
18-19	0.64	38	106	34	5.4	34	3.48	4.01	10.70
19-20	0.68	36	106	25	4.4	34	3.43	4.07	10.26
24-25	0.56	35	110	32	6.3	54	4.18	4.36	10.18
29-30	0.65	14	96	30	5.6	88	4.80	4.57	10.10
33-34	0.53	13	103	26	4.8	61	4.77	4.70	10.56

Table I:

Trace metals, iron, organic carbon and alumina in near surface sediments.

Spuremetalle, Eisen, organischer Kohlenstoff und Al₂O₃ in oberflächennahen Sedimenten aus dem Bornholm Becken.

Tabelle I:

Bornholm Basin sediments

Core KI-878 = GPI 10193-2

Lab. no.	Depth below surface (cm)	Libby age + 10, B.P. (yr B.P.)	$^{13}\text{C}_{\text{(PDB)}}$ (‰)
878.01	0 - 1	490 + 180	-25.7
878.02	1 - 2	830 + 160	-24.7
878.03	2 - 3	1330 + 120	-26.1
878.04	3 - 4.5	1450 + 80	-25.2
878.05	4.5-6	1515 + 60	-25.6
878.06	6 - 7	1380 + 50	-25.1
878.07	7 - 8	1465 + 75	-25.3
878.08	8 - 9	1640 + 75	-24.9
878.09	9 - 10	1810 + 85	-25.6
878.10	12 - 13	1440 + 60	-24.3
878.11	13 - 14	1330 + 60	-24.2
878.12	14 - 15	1300 + 50	-24.6
878.13	15 - 16	1200 + 60	-23.6
878.15	17 - 18	1230 + 60	-24.2
878.17	19 - 20	1320 + 85	-26.1
878.18	24 - 25	1420 + 80	-24.8
878.19	29 - 30	1730 + 50	-25.1
878.20	33 - 34	1985 + 60	-24.7

Table II:

 ^{14}C and $\delta^{13}\text{C}$ values of near surface sediments. ^{14}C und $\delta^{13}\text{C}$ Werte von oberflächennahen Sedimenten aus dem Bornholm Becken.

Tabelle II:

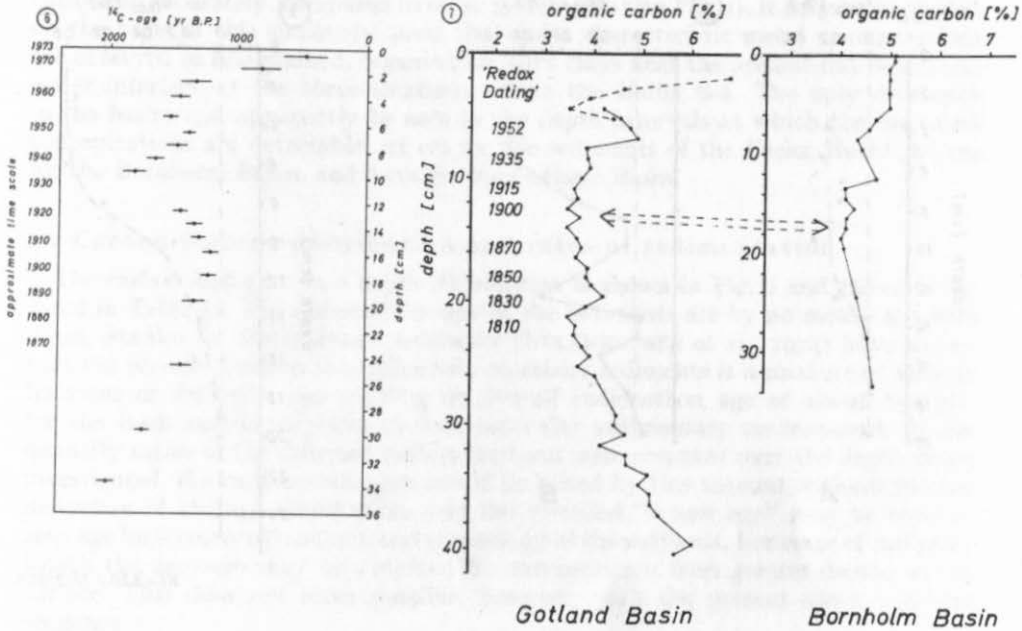


Fig. 6:

¹⁴C-age-vs.-sediment depth in core KI-878 (= GPI 10193-2) from the Bornholm Basin at 71 m of water depth. The approximate time scale is based on a constant dry matter supply of 760 g/m²·yr.

¹⁴C-Alter in Abhängigkeit von der Tiefe im Sedimentkern KI-878 (= GPI 10193-2) aus dem Bornholm Becken, 71 m Wassertiefe. Die absolute Zeitskala ist unter der Annahme einer konstanten Trockensubstanzzufuhr von 760 g/m²·Jahr errechnet, unter Berücksichtigung des Wassergehaltes.

Abb. 6:

Fig. 7:

Distribution of organic carbon with depth (A) for the Gotland Basin and (B) for the Bornholm Basin. Values in Fig. (A) are from Niemistö & Viopio (1974); dashed line = core from 1971, solid line = average of cores from 1970 and 1971. The similarity of the organic carbon distributions with depths indicates similar influences in both sedimentary environments, so that the lowest organic carbon contents are believed to be deposited at the same time in their respective basins.

Variation des C_{org}-Gehaltes mit der Tiefe: (A) für Sedimente aus dem Gotland Tief und (B) für Sedimente aus dem Bornholm Becken. Die Werte in (A) entstammen der Arbeit von Niemistö und Voipio (1974): gestrichelt: Kern von 1971, ausgezogen: Mittel der C_{org}-Werte der Kerne von 1970 und 1971. Die Ähnlichkeit der C_{org}-Profile aus beiden Becken deutet auf überregionale Einflüsse hin. Es wird hier angenommen, daß die Sedimente mit geringstem C_{org}-Gehalt zur gleichen Zeit, etwa um 1900, abgelagert wurden.

Abb. 7:

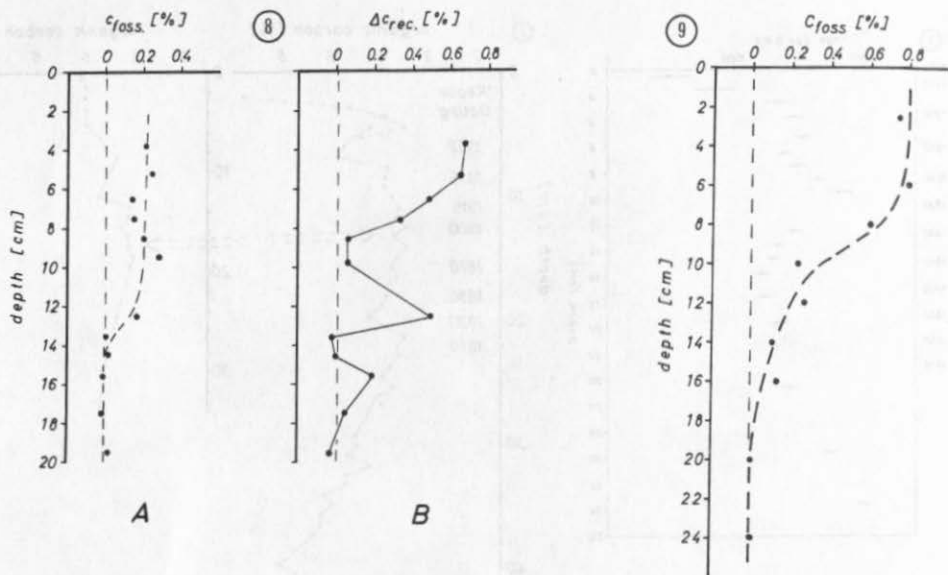


Fig. 8:

Reduction of organic carbon excess above the average carbon content to fractions of different ^{14}C -activities at approx. 17 cm of sediment depth: (A) fossil fraction C_{foss} and (B) residual "recent" fraction C_{rec} with ^{14}C -activities being 0% STD and 99% STD, respectively. Amounts of carbon refer to total dry matter of sediment samples. The total organic carbon content at the reference depth is 4.1% and is assumed to have a constant ^{14}C -activity of 85.3% STD, or 1280 yrs. on the radiocarbon time-scale, up to the sediment surface.

Die Aufteilung des organischen Kohlenstoffs in Fraktionen unterschiedlichen ^{14}C -Gehalts (A) fossile Fraktion C_{foss} und (B) Zuwachs C_{rec} an rezemem C_{org} gegenüber den Sedimenten bei 17 cm Tiefe. Die Kohlenstoffmengen beziehen sich auf das Trockengewicht. Die entsprechenden ^{14}C -Aktivitäten der Fraktionen (A) und (B) sind 0% STD und 99% STD. Die Sedimente in 17 cm Tiefe, auf die hier Bezug genommen wird, haben einen C_{org} -Gehalt von 4.1% und eine ^{14}C -Aktivität von 85.3% STD entsprechend einen ^{14}C -Alter von 1280 Jahren. Es wird hier vorausgesetzt, daß dieser „Untergrund“ in den Sedimenten bis zur Oberfläche gleich geblieben ist.

Fig. 9:

Fossil organic carbon content (on dry weight basis) in core KI-620 (= GPI 11666) from the Kieler Bucht. The figures were calculated from the ^{14}C -age deviation from a linear sedimentation model as obtained for the sediments below 20 cm of depth (Erlenkeuser et al., 1974). The sedimentation rate is 1.4 mm/yr. Data may scatter by about 0.08% on dry weight basis due to possible variations of the "recent" fraction, which, however, were not taken into account here. Fossil carbon flux to the Kieler Bucht sediments is about 2 times higher than in the Bornholm Basin.

Fossiler organischer Kohlenstoff (in Prozent der Trockensubstanz) im Kern KI-620 aus der Kieler Bucht. Die Werte wurden aus der Abweichung der ^{14}C -Alter von dem Modell eines linearen Sedimentzuwachses berechnet, welches für den Kernabschnitt unterhalb von 20 cm Sedimenttiefe gültig ist. Die Sedimentationsrate beträgt 1.4 mm/Jahr. Mögliche Variationen des Anteils von „rezemem“ Kohlenstoff, die hier nicht berücksichtigt wurden, können Fehler von ca. 0.08% der Trockensubstanz bedingen. Die Ablagerungsrate des fossilen Kohlenstoffs ist in der Kieler Bucht etwa doppelt so groß wie im Bornholm Becken.

Abb. 8:

Abb. 9:

KI-620 / 12.3.1975

easily and accurately, compared to other metals (see also Fig. 1), it may be suggested on the basis of this similarity alone that quite characteristic metal concentrations are observed in fine-grained, organic-rich, silty clays near the present-day sediment/water interface at the three locations within the Baltic Sea. The only difference in the basins can apparently be seen in the depth intervals at which the increased concentrations are detectable: 22 cm for the sediments of the Kieler Bucht, 16 cm for the Bornholm Basin, and 6 cm for the Gotland Basin.

4.2 Carbon isotope distribution and rates of sedimentation

The carbon isotope - vs. - depth distribution is shown in Fig. 6 and the data are listed in Table II. The radiocarbon ages of the sediments are by no means absolute dates. Studies on Kieler Bucht sediments (ERLENKEUSER et al., 1974) have shown that the organic fraction in argillaceous nearshore sediments is a mixture of various fractions of different ages yielding an overall radiocarbon age of about 850 yrs. for the fresh surface deposits in this particular sedimentary environment. If the quantity ratios of the different carbon fractions were constant over the depth range investigated, the radiocarbon ages would be raised by this amount without further distortion of the age distribution, and the so-called "recent age" may be used as zero-age for a corrected radiocarbon chronology of the sediment. For cores of sufficient length the zero-age may be obtained by extrapolation from greater depths to the surface. This does not seem possible, however, with the present short box-core sequence.

A crude age estimate is obtained, however, from comparison of the present results with previous investigations in the Kieler Bucht. The similarity of the distributions of heavy metals and of radiocarbon with depth suggests that the samples from the Bornholm Basin are from the 19th and 20th century. The sharp decrease of the ^{14}C -ages in the uppermost layers very likely reflects the input of radiocarbon which has been artificially produced by fusion bomb tests in the atmosphere (e.g. VOGEL, 1972; WILLKOMM, 1974) and has subsequently been about 1960 entered the hydrosphere (GULLIKSEN and NYDAL, 1972). The corresponding sedimentation rate for the upper layers is therefore 2 to 3 mm/yr.

Another age estimate is based on the variation of the organic matter content with depth. There is a pronounced minimum in organic carbon at depths between 14 to 20 cm. NIEMISTÖ and VOIPIO (1974) found a similar distribution in a sediment core from the Gotland Basin. These authors present evidence that climatic variations might have influenced the productivity and the decomposition rate of organic matter in the surface layer of the Baltic Sea and thus caused variations of the organic carbon content of the sediments. Accepting this view, the Bornholm Basin deposits should have been effected in the same manner.

This is supported by the slight increase of the stable carbon isotope ratio, observed in that depth range, which parallels the decrease of organic carbon (Tab. II). It may indicate elevated water temperatures during plankton production (SACKETT et al., 1965; DEGENS et al., 1968). In addition a lower input of land-derived plant debris (with a $\delta^{13}\text{C}$ of about -25‰) would further increase the $^{13}\text{C}/^{12}\text{C}$ -ratio towards that of marine plankton, which should have a $\delta^{13}\text{C}$ of around -20‰ or slightly above. The latter figure is estimated from a ^{13}C content of 0‰ for the bicarbonate fraction of recent Baltic Sea surface water at about pH 8 (ERLENKEUSER et al., 1975) taking into account an isotope fractionation of about -19‰ during plankton formation (DEGENS et al., 1968).

According to NIEMISTÖ and VOIPIO (1974) the lowest organic carbon contents occurred at about A.D. 1900 (Fig. 7). With this date then, an average sedimentation rate of 2.4 mm/yr and a dry matter supply of 760 g/m²/yr. is calculated for the Bornholm sediments above 17 cm of depth. An approximate time scale was calculated from this figure, assuming that the dry matter supply has remained essentially constant over that depth range.

Below 20 cm of depth the sedimentation rate as deduced from the ¹⁴C-dates seems unreasonably low. This might be due to a varying age composition of the organic fraction and, in turn, be associated with the changing climatic conditions during the 16th and 17th century which probably favored erosional events by stronger waves and bottom currents.

5. Interpretation

The interpretation of our findings follows in general the ideas on anthropogenic effects through fossil fuel residues as previously outlined for the sediments of the Kieler Bucht. This is by no means the only possibility and the data might be understood in other terms, if more becomes known on recent sedimentological processes. However, it is still our aim to apply this working hypothesis to different sedimentary basins of the Baltic Sea.

5.1 Carbon isotope distribution

The inversion of the ¹⁴C age-distribution at a depth of about 16 cm coincides with the beginning of the heavy metal increase and may thus reflect an increasing supply of coal residues, as previously discussed. Accordingly, the radiocarbon age at depths of about 16 to 20 cm should then be essentially free of anthropogenic effects and should represent the natural ¹⁴C activity of the sediment. The apparent ¹⁴C age is about 400 yrs. older than in Kieler Bucht sediments.

Above 14 cm of sediment depth the organic carbon gradually increases towards the surface. Though anthropogenic effects become more pronounced in that depth range, the increasing amount of organic carbon cannot be caused only by a supply of coal residues, since the observed increase of the radiocarbon dates is far too small; a fossil carbon addition of 20% of the total organic carbon will change the ¹⁴C age by about 1800 yrs. Apart from this, a small fraction of the carbon must therefore be supplied from another source, either from the marine environment or from the terrestrial biosphere. The stable carbon isotope ratios give a slight indication of land-derived plant debris as being the more important source. A higher marine productivity or incomplete bacterial decomposition should increase the $\delta^{13}\text{C}$ values rather than decrease them, but reduced water temperatures and/or diagenetic effects might also produce small isotope fractionations in the observed direction (DEGENS et al., 1968).

The radiocarbon dates indicate that the additional organic carbon, at least in part, is of recent age. It is seen from Fig. 6 that above 10 cm of sediment depth, any natural input of old carbon potentially associated with the increased clay mineral content, or of fossil carbon probably supplied to the sediments along with the heavy metals, is apparently overwhelmed by young organic matter. In this case it is unimportant whether the fraction is land-derived or of marine origin, since both sources have essentially the same ¹⁴C levels within the 20th century with the exception of the last decade.

On the basis of these findings, the organic carbon of the sediments may be understood as composed of three fractions:

- 1) an "eroded" fraction of unknown but low ^{14}C activity causing the high zero-age of the sediment as a whole. This fraction is probably associated with the allochthonous inorganic sediment fraction.
- 2) an "authigenic or recent" carbon fraction, i.e. organic carbon with the respective recent activity of the date of its deposition,
- 3) a "fossil" carbon fraction mobilized through man's activity.

In a first approximation radioactive decay and atmospheric ^{14}C variations affecting the recent activity of the respective "authigenic" fraction may be neglected. Since nothing is known about the ratio of the "eroded" and "authigenic" fractions nor about the ^{14}C activity of the eroded fraction, the sediments at a depth of about 17 cm, which are presumably free of anthropogenic effects, will be used for reference. This assumes that the content and ^{14}C activity of the "eroded" carbon fraction have remained essentially constant during depositional history. By setting up the balance equations for the organic carbon and radiocarbon, it is then possible to divide the carbon in excess to the minimum carbon content into an "authigenic" and a "fossil" fraction for each depth interval so that their combined ^{14}C activities and carbon contents add up to those of the respective sediment sample.

The results shown in Fig. 8 indicate an increasing amount of "authigenic" carbon towards the sediment surface, while the "fossil" carbon is rather constant in the upper part of the core. The same feature is seen in the distribution of heavy metals. For comparison the concentration of the "fossil" carbon fraction in Kieler Bucht sediments is shown in Fig. 9. If the different sedimentation rates in the two basins are taken into account, the flux of "fossil" carbon to Kieler Bucht sediments is about twice as high as in the Bornholm Basin, whereas, for comparison, the input of anthropogenic Zn seems to be the same in these basins (see below). This may indicate that the pollution load is a complex aggregation of different constituents with correspondingly different responses to transport processes.

The ^{14}C -activities of the uppermost samples are affected by artificial radio-carbon from the fusion bomb tests in the atmosphere. At present, the level of activity of the Baltic surface water, and hence of the authigenic organic matter, is about 1.43 times higher than the pre-bomb level (ERLENKEUSER et al., 1975). The residence time of a CO_2 molecule in the surface layer, with respect to exchange with the atmosphere, is about 10 yrs., and numerical calculations further indicate that the ^{14}C -activity has been at the present level for the past few years. If, in the same manner, the ^{14}C -activity of the sediment surface layer reflects a (quasi-)stationary state, then the activity of the sediment as a result of the increased ^{14}C -content of the authigenic organic matter makes possible an estimate of the relative concentration of the "authigenic" carbon fraction. The present data indicate that the "authigenic" carbon amounts to about one quarter of the organic carbon if a constant amount of "fossil" carbon contaminates the upper sediment layers. The corresponding flux of "authigenic" organic carbon from the water column into the sediment is in the order of 10% of the primary production in the southern Baltic Sea (RENKE et al., 1974). The apparent ^{14}C -age of the "eroded" fraction is calculated at about 1520 years.

5.2 Metal distribution

Recounting the similarity of the relative increases of cadmium, lead, zinc, and copper in the uppermost sediment layers and the characteristic association of these

elements in residues of fossil fuel, particularly in coal-ash, it is suggested here again that man's increased mobilization of these constituents is reflected in the increase of metals in near-surface sediments; for a detailed discussion see ERLÉNKEUSER et al. (1974). This interpretation has been confirmed by the recent findings of FÖRSTNER & REINECK (1974) who showed that anthropogenic metal input may also be found in sediments deposited during the last 100 to 200 years in the Deutsche Bucht area of the North Sea. Apart from the data presented here by the carbon isotope composition to support the above interpretation, further evidence is also presented in the form of a more precise differentiation of the anthropogenic and natural (= minerogenic) fractions of the metal fluxes in the three Baltic Sea sedimentary basins.

5.2.1 Zinc flux

Since it appears from analytical considerations that the distribution of zinc in these basins can be more precisely determined than the distribution of the other metals, calculation and discussion of fluxes shall be restricted to those of zinc. Fig. 9 shows time-flux profiles for zinc for the three basins, taking into account different sedimentation rates, the zinc and water contents of the sediments, and a constant background of minerogenic input. The sedimentation rates are between 1.3 and 2.0 mm/yr for the Gotland Basin (NIEMISTÖ and VOIPIO, 1974), 2.2 to 3.3 mm/yr for the Bornholm Basin, and 1.4 mm/yr for the Kieler Bucht. The zinc contents are listed in Table I, and the water content of the sediment core from the Bornholm Basin is illustrated in Fig. 9 — the line indicates a generalized water distribution which was used for the flux-time profiles of all three basins (mg H₂O/100 mg of dry sediment). 115 ppm was used to represent background minerogenic zinc input, which corresponds to a flux of about 70 mg/m² · yr. From these data the total zinc flux was calculated as follows:

$$\text{Zn flux (mg} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}) = \left[\left(\frac{1}{\rho} \cdot \frac{\text{mg Zinc}}{100 \text{ g Sediment}} \right) + \frac{\text{ml Pore water}}{100 \text{ g Sediment}} \right] \cdot R$$

R = Rate of sedimentation

ρ = Dry density, 2.54 g · cm⁻³

It is most important to note from Fig. 10 that the present-day anthropogenic zinc flux is constant at about 100 mg/m² · yr for all three basins and that there is an increasingly longer time needed to achieve the same rates of zinc flux in the increasingly older sediments of the Kieler Bucht, of the Bornholm and Gotland Basins, respectively. This emphasizes the point that in addition to the constant natural, minerogenic source of zinc a second fluctuating "hydrogenous" source may be postulated which appears earlier to have been spreading more slowly north-eastwards from the Belt Sea to the Gotland Basin and which today is affecting the entire area at the same rate. The "hydrogenous" source of additional Zn (= here the waters of the Baltic Sea) is postulated by the relationship between Zn in the sediments and rates of sedimentation. The surface sediments of the three basins have significantly different Zn contents (Kieler Bucht 350 ppm, Bornholm Basin 250 ppm, Gotland Basin 500 ppm (Figs. 4, 5, 6) which are entirely a function of dilution by sediment input. This may be seen from the constant rates of Zn-flux calculated from the amount of Zn and the rate of sedimentation, two independently established parameters. In our present interpretation this "hydrogenous" source

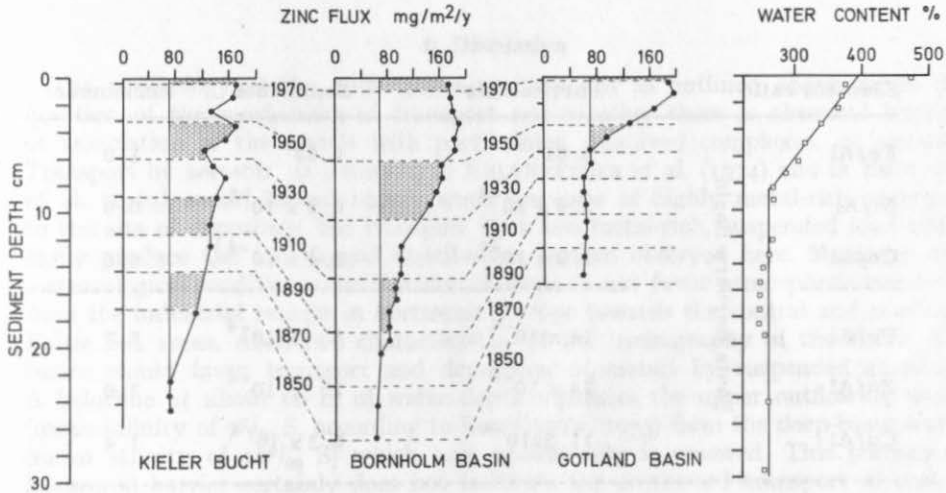


Fig. 10:

Abb. 10:

Annual Zn flux to the Kieler Bucht, the Bornholm Basin, and the Gotland Basin; the data are calculated from sedimentation rates and Zn contents of the sediments as determined by Erlenkeuser et al. (1974), by Niemistö and Voipio, (1974), and reported here; furthermore a general profile of water contents with sediment depth was used for these calculations as shown here for the Bornholm sediments. The natural Zn flux of $70 \text{ mg/m}^2 \cdot \text{yr}$ is indicated as background; anthropogenic Zn flux can be seen by the deviation of total input from the background flux.

Die Ablagerungsraten von Zn in der Kieler Bucht, im Bornholm Becken und im Gotland Tief. Die Werte wurden aus den Sedimentationsraten und den Zn-Konzentrationen berechnet (Erlenkeuser et al., 1974, Niemistö und Voipio, 1974, und diese Arbeit). Dabei wurde die Variation des Wassergehaltes mit der Tiefe berücksichtigt, wie sie für die Sedimente des Bornholm Beckens gemessen wurde. Die natürliche Zufuhr von Zn beträgt $70 \text{ mg/m}^2 \cdot \text{Jahr}$. Der darüberhinaus gehende Betrag wird als anthropogene Zufuhr angesehen.

Element ratio	Particulates	Sediments	Enrichment
Fe/Al	0.61	0.63	1.0
Ni/Al	5.9×10^{-4}	6.9×10^{-4}	0.9
Co/Al	1.9×10^{-4}	3.4×10^{-4}	0.6

Pb/Al	14×10^{-4}	6×10^{-4}	2.3
Zn/Al	74×10^{-4}	25×10^{-4}	3.0
Cu/Al	11.3×10^{-4}	8.3×10^{-4}	1.4

Fe/SiO ₂	4.9×10^{-2}	4.0×10^{-2}	1.2

Zn/SiO ₂	6.3×10^{-4}	3.3×10^{-4}	1.9
Pb/SiO ₂	2.9×10^{-4}	0.9×10^{-4}	3.1

Data from Santa Barbara Basin are by BRULAND et al. (1974) and from the Western Baltic Sea by KUJERS (1974).

Table III:

Elemental ratios of metals to aluminium and to silica in particulate and sediment material from the Santa Barbara Basin and the Western Baltic Sea.

Verhältnisse ausgewählter Metalle zu Aluminium und zu Kieselsäure in partikulärer Substanz und in Sedimenten aus dem Santa Barbara Basin und aus der westlichen Ostsee.

Tabelle III:

of heavy metals is ultimately controlled by anthropogenic mobilization and this source suggests the transport mechanism. The other heavy metals, cadmium, lead, and copper, have the same pattern of flux through time although the uncertainties are much larger, due to possible variations in the respective minerogenic fluxes. It should be pointed out that in spite of the good analytical data for zinc, the varying water contents and rates of sedimentation are reflected in the calculated fluxes with an uncertainty of $\pm 20 \text{ mg/m}^2 \cdot \text{yr}$.

6. Discussion

The chronology of the anthropogenic zinc input as outlined above raises the question of the mechanism of transport and whether there is chemical binding or association of the metals with particulates, dissolved complexes, or aerosols. Transport by aerosols, as discussed in ERLÉNKEUSER et al. (1974) and in BRULAND et al. (1974) would indeed supply small amounts of highly metal-rich materials to the site of deposition but transport by a less metal-rich, suspended load could easily produce the time-lagged distribution pattern observed here. Moreover, the meteorological conditions over Northern Europe do not favor atmospheric transport from the industrial centers in northwest Europe towards the central and northern Baltic Sea areas. Also, two characteristics of the hydrography of the Baltic Sea basins would favor transport and deposition of metals by suspended material: A halocline at about 60 m of water depth separates the upper outflowing water (mean salinity of 7‰ S, according to SEN GUPTA, 1973) from the deep-basin water (mean salinity of 17‰ S) which only occasionally is renewed. This permanent horizontal barrier certainly does not facilitate the downward transport of metals as required in the wash-out of aerosols in precipitation. On the other hand, metals could be readily transported in the suspended load or in the dissolved state along the bottom from the Belt Sea to the Bornholm Basin and on to the Gotland Basin.

WYRTKI (1954), FONSELIUS (1962; 1969), and others have described such deep water movements in the Baltic Sea basins. Although salt water flows in from the North Sea much more frequently than the time lag observed with the zinc distribution would suggest, the intensity and duration of the inflows are extremely varied, so that it might take several inflows over a period of time to transport enough metal-rich particulates into the basins. There is an enrichment of lead, zinc, and copper in the composition of present-day particulates in inshore waters, compared to the underlying sediment, but no such enrichment of iron, cobalt and nickel. Pre-industrial particulates for comparison to determine an absolute increase in particulate metals are hard to come by and the composition of those from far off-shore might be controlled by other factors. Table III shows various metal-to-aluminium ratios of particulates from Californian coastal waters, as reported by BRULAND et al. (1974), and the metal-to-silica ratios of particulates for the Western Baltic Sea, as reported by KUIJPERS (1974), compared to the ratios found in sediments.

A second possibility for explaining the time-lagged distribution pattern could be related to the increasing distance of the three depositional sites from land. The Kieler Bucht sediment core was taken at a distance of less than 2 km from shore, that of the Bornholm Basin approximately 50 km, and the core from the Gotland Basin was between 100 and 150 km from the Swedish and USSR land areas. As pointed out earlier, transport of the additional zinc directly from shore to the accumulation sites would have to be closely related to the transport of other terrigenous sediment fractions and would not agree with the evidence for a "hydro-

geneous" source. Mainly for this reason, the increased distance from land does not seem a likely explanation for observed zinc-distribution pattern.

How the particulates acquire their metals remains open to speculation. Whether they scavenge dissolved components from the seawater, or whether they simply come from river run-off or aerosol wash-out particles, all of which would preferentially involve man-mobilized metals, is subject to further investigation such as that in progress at the Laboratorium für Sedimentforschung, Heidelberg (BANAT et al., 1974). Perhaps at the present time the knowledge about anthropogenic metals in the sedimentary record is better than the knowledge of how they got there. The answer to this is probably not one all-important process, but rather is related to many mechanisms of transport, fixation and deposition which are operative in various environments. One of these environments might be represented by the conditions encountered in the basins of the Baltic Sea.

7. Acknowledgements

We would like to acknowledge the expert technical assistance in sample treatment, mass spectrometric analyses, counter operation, and metal and alumina analyses which we received from M. GUMZ, H. METZNER, H. FINN, H. MÖLLER and M. WHITICAR. For discussion and helpful comments we would like to thank F.-C. KÖGLER and H. WILLKOMM. We are further grateful to the Deutsche Forschungsgemeinschaft for financing this research under the Sonderforschungsbereich 95 at the Universität Kiel, the Fraunhofer Gesellschaft for help in operation of the R.V. PLANET during Baltic Cruise 5/1974, and the University Computer Center for data processing.

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Manuskript eingegangen am 17. 3. 1975