

On the Alkalinity of Baltic Waters

By

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Introduction

According to the definition given by HELLAND-HANSEN, JACOBSEN, and THOMPSON (1948) the alkalinity is "the quantity of anions, excepting those of strong acids" contained in 1 litre of sea water at 20°C. As is well known, the most important "non-strong" acids are carbonic acid and boric acid. While in oceanic water the alkalinity is closely proportional to the chlorinity, this is not true of Baltic water. The linear relationship existing between the two quantities here contains a constant term which is due to the influence of the great quantities of river water of varying composition flowing into the Baltic. Some of the affluents, passing through areas of primitive rocks, are practically lime-free while others transport high amounts of carbonates into the sea. It is therefore natural that different equations relating the alkalinity and the chlorinity are valid in different parts of the Baltic. These equations, however, vary from year to year and, in addition, single alkalinity values never fit well into any equations, two facts which indicate that the amount of carbonates in the water also varies, carbonate and bicarbonate ions being the principal anions of "non-strong", i. e. weak acids in the water. If these conclusions are correct the amount of calcium and magnesium ions should also vary, since the excess of carbonate ions are furnished by the solution of calcium and magnesium carbonates. But contrary to expectations, both calcium and magnesium have been found to be regularly distributed. The calcium concentrations in the different basins fit well into linear equations, which do not vary from year to year, while the magnesium concentrations are, on an average, directly proportional to the chlorinities over the whole of the Baltic, the ratio being the same as for oceanic water. This shows that the explanation given above for the variations of the alkalinity is not sufficient. There must exist in Baltic water other anions of weak acids, which have their own rhythm of variation and which seemingly erratically influence the alkalinity values. In the present paper the assumption is put forth that organic acids here reveal their presence. An attempt is made to evaluate in milliequivalents the amounts of these non-accounted-for anions in a number of samples from eight stations in the Gulf of Bothnia and the Baltic proper. The unknown anions, which of course may be of more than

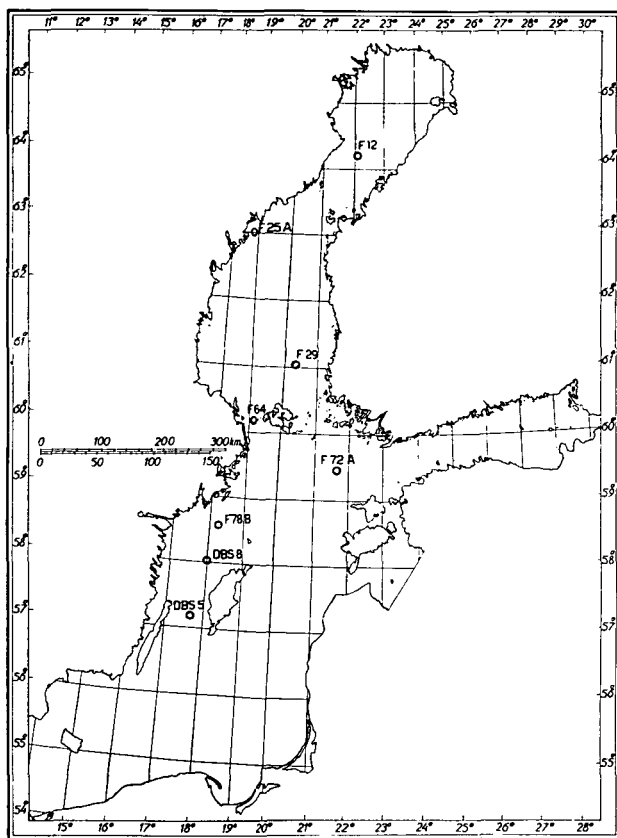


Figure 1. Hydrographical stations.

one kind, are designed by a common name as the “surplus alkalinity”. It is suggested that part or the whole of it may be formed of complex anions of organic decomposition products coupled with boric acid. It should be pointed out that the surplus alkalinity is not identical with the total organic matter in Baltic water, but may perhaps serve as a rough measure thereof in that a high surplus alkalinity may indicate a high amount of organic matter.

Samples and Analyses

During the regular summer cruises organized in June 1957 by the Marine Research Institute of Helsinki on board the research ship “Aranda”, 65 water samples to be analysed for alkalinity were collected from 8 stations in the Gulf of Bothnia and in the Baltic proper (Figure 1).

The samples were analysed by indirect titration. To 100 ml of water 15 ml of 0.012-n HCl were added. The CO_2 set free was expelled by passing CO_2 -free air through the solution for at least half an hour after which the excess acid was titrated with 0.012-n NaOH, methyl red (0.1 g of the Na salt dissolved in

100 ml of ethyl alcohol) being used as indicator. Electrometric titrations using the Beckman pH-meter and in the presence of the indicator, showed that the equivalence point coincided with the appearance of the purely alkaline colour. For accurate results it is convenient to use as a colour standard an alkaline solution with the same indicator concentration as in the analysis (see, however, the discussion on the equivalence point, p. 18). The alkalinity values in milliequivalents per litre were reduced by calculation to milliequivalents per kilogramme of sea water. The accuracy of the titration thus performed may be evaluated at \pm one drop or \pm 0.004 meq/kg. This corresponds to 0.25–0.50% of the alkalinity.

Thirteen surface and bottom samples were titrated electrometrically and at the same time analysed for boron. When the alkalinity titration was ready 5 g of mannitol were added and the titration continued. The mean equivalence point for the thirteen samples was pH 7.37, the range being 7.15 to 7.67.

Results

The results of the analyses are presented in Table 1. Columns 1, 2, and 3 give the depths in metres, Cl ‰ and the alkalinity in meq per kg respectively,*) columns 6 and 7 the boron concentrations in mg-at per kg or, what amounts to the same, H₃BO₃ meq/kg and the ratio B/Cl. Boron seems to occur in a slightly higher concentration in the Baltic than in the oceans. The mean ratio of B mg-at/kg to Cl ‰ for the 13 analyses is 0.0244, corresponding to $B^{0/00}/Cl^{0/00} = 0.000264$ or $H_3BO_3^{0/00}/Cl^{0/00} = 0.00151$. LYMAN and FLEMING's "present best value" for the last ratio is 0.00137 (quoted after BARNES (1955)).

The alkalinities are shown graphically in Figures 2a and b (p. 10). Here the depth coordinate is the same for all stations, but the origins of the chlorinity and the alkalinity value are successively displaced towards the right. It is seen that the alkalinities, as expected, on the whole follow the chlorinities. It is, however, noteworthy that at four stations, F25A, F29, F64, and DBS5 there is a slight decrease of the alkalinity at the bottom though the corresponding chlorinities increase or remain constant. At F64 this decrease is felt already at 25 m from the bottom. The decrease at DBS5 is perhaps only apparent and due to the exceptionally and maybe accidentally high alkalinity at 80 m. A duplicate analysis on a smaller amount of water, however, confirmed the high value. In general, it was not possible to make duplicate analyses owing to the small volume of the samples.

Discussion

The small number of stations does not allow the computation of equations expressing the relationship between the alkalinity and the chlorinity and in view of the fact that Baltic alkalinity values are always more or less scattered and never agree well with calculated linear equations, such a computation would not offer much interest. The general equations calculated by BUCH

*) The chlorinity for F12, 0 m, has been changed. It was 1.73 ‰, a value which agreed neither with the alkalinity, nor with the boron content. At this station the sample for 80 m was titrated electrometrically, not the bottom sample.

Table 1
Analyses of alkalinity and boron in Baltic water

Depth in metres 1	Chlorinity 2	Alkalinity 3	Minimum alkalinity 4	Surplus alkalinity 5	B 6	7
m	Cl‰	Alk meq/kg	Alk _{min} meq/kg	Alk _x meq/kg	mg-at/kg H ₂ BO ₃ meq/kg	B/Cl
F12, 64°03' N, 22°04' E						
0	1.96	0.811	0.744	0.067	0.048	0.0245
20	1.96	0.812	0.744	0.068		
40	2.05	0.854	0.774	0.080		
60	2.32	0.937	0.863	0.074		
80	2.42	0.971	0.896	0.075	0.058	0.0240
110	2.55	1.006	0.939	0.067		
F25A, 62°59.5' N, 18°51' E						
0	2.97	1.157	1.078	0.079	0.069	0.0232
20	3.13	1.212	1.131	0.081		
40	3.28	1.266	1.181	0.085		
60	3.49	1.321	1.250	0.071		
80	3.67	1.373	1.310	0.063		
100	3.68	1.372	1.313	0.059		
150	3.74	1.389	1.333	0.056		
175	3.75	1.392	1.336	0.056		
189	3.75	1.381	1.336	0.045	0.096	0.0256
F29, 61°03' N, 20°16' E						
0	3.25	1.242	1.171	0.071	0.084	0.0258
20	3.24	1.239	1.167	0.072		
40	3.32	1.263	1.194	0.069		
60	3.32	1.293	1.194	0.099		
80	3.64	1.361	1.300	0.061		
100	3.76	1.355	1.340	0.015	0.094	0.0250
F64, 60°11.5' N, 19°09' E						
0	3.09	1.211	1.118	0.093	0.074	0.0240
20	3.33	1.277	1.197	0.080		
40	3.69	1.392	1.316	0.076		
60	3.76	1.425	1.340	0.085		
80	3.84	1.448	1.366	0.082		
100	3.86	1.438	1.373	0.065		
150	3.92	1.439	1.393	0.046		
200	3.98	1.461	1.412	0.049		
250	3.99	1.435	1.416	0.019		
275	4.00	1.414	1.419	-0.005	0.094	0.0235
F72A, 59°27' N, 21°49' E						
0	3.50	1.382	1.225	0.157	0.079	0.0226
20	3.85	1.428	1.306	0.122		
40	4.00	1.464	1.341	0.123		
60	4.46	1.507	1.448	0.059		
80	5.69	1.610	1.471	0.139		
100	5.91	1.634	1.485	0.149		
125	5.95	1.642	1.487	0.155	0.151	0.0254

Table 1 (continued)

Depth in metres	Chlorinity	Alkalinity	Minimum alkalinity	Surplus alkalinity	B	7
1	2	3	4	5	6	
m	Cl ^{0/00}	Alk meq/kg	Alk _{min} meq/kg	Alk _x meq/kg	mg-at/kg H ₂ BO ₃ meq/kg	B/Cl
F78B, 58°36' N, 18°15' E						
0	3.50	1.308	1.225	0.083	0.084	0.0240
20	3.78	1.387	1.290	0.097		
40	3.96	1.418	1.332	0.086		
60	4.29	1.494	1.408	0.086		
80	5.61	1.630	1.467	0.163		
100	5.81	1.638	1.479	0.159		
150	6.00	1.640	1.490	0.150		
200	6.04	1.634	1.492	0.142		
250	6.04	1.656	1.492	0.164		
300	6.11	1.662	1.497	0.165		
350	6.11	1.650	1.497	0.153		
400	6.14	1.658	1.498	0.160		
425	6.16	1.663	1.500	0.163	0.148	0.0240
DBS8, 58°00.5' N, 18°01' E						
0	3.68	1.396	1.267	0.129	—	—
20	3.85	1.400	1.306	0.094		
40	3.98	1.456	1.336	0.120		
60	4.25	1.457	1.399	0.058		
80	5.53	1.555	1.462	0.093		
100	5.77	1.609	1.476	0.133		
150	5.88	1.619	1.483	0.136		
186	5.88	1.638	1.483	0.155	—	—
DBS5, 57°09' N, 17°40' E						
0	3.94	1.427	1.327	0.100	0.101	0.0256
20	3.95	1.453	1.329	0.124		
40	4.02	1.458	1.346	0.112		
60	4.39	1.530	1.431	0.099		
80	5.51	1.650	1.461	0.189		
105	5.71	1.615	1.473	0.142	—	—

(1945, p. 90) give too high values all through, but neither is in good agreement to be expected as is shown by the equations for the separate years (1932–1936) which vary considerably. It may be argued and probably with a certain justification that the bad agreement might be due to the difference in method, my samples having been treated with CO₂-free air at room temperature for expelling the carbon dioxide liberated by the acid whereas boiling was used for the older material. This circumstance, however, can only account for a fraction of the deviations observed. The principle explanation must be sought elsewhere. It is also worth mentioning that the air current method was used on 75 samples from the Barents Sea and they gave on an average the same relation between the alkalinity and the chlorinity as is accepted for Atlantic water, viz., Alk meq/l = 0.123 Cl^{0/00} (WATTENBERG, 1933).

It is well known that the alkalinity is much higher in the Baltic compared with the chlorinity than in oceanic water. This is ascribed to bicarbonates and carbonates brought down by river water, but may also in part be due to anions of organic acids transported by rivers or formed as a result of the metabolism within the sea.

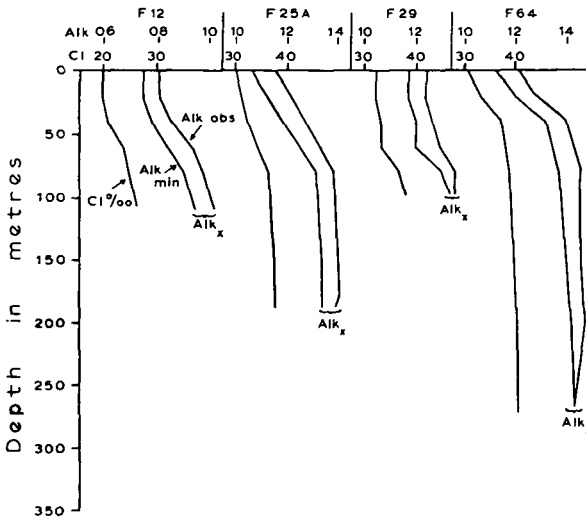


Figure 2a. Variation with depth of the chlorinity and the minimum, observed and surplus alkalinities at the Gulf of Bothnia stations.

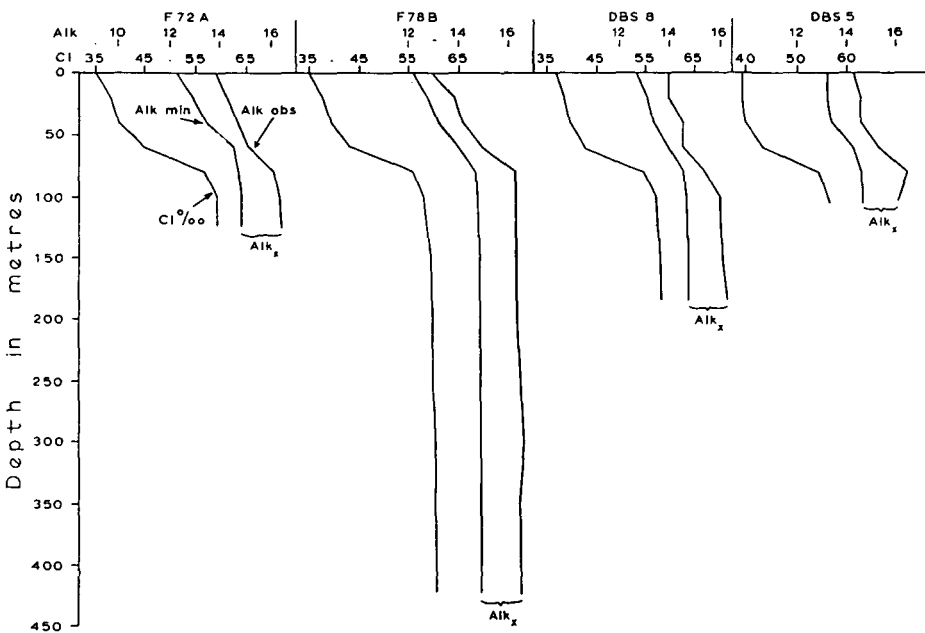


Figure 2b. Variation with depth of the chlorinity and the minimum, observed and surplus alkalinities at the Baltic proper stations.

The organic matter brought to the sea by rivers is far from negligible. On the basis of Swedish, Finnish and to a certain extent, Russian and Estonian analyses of river water the author (GRIPENBERG, 1934) calculated the mean annual addition of organic matter to the Baltic at 12.2 million tons—determined as ignition loss on evaporation residue of filtered water—corresponding to almost 60 g per square metre of sea surface. The greater part thereof is in colloidal solution and nothing is known of the amount that becomes chemically dissolved in the water. The end product of the mineralization, the carbonic acid in its various forms, is accessible to analysis, not so the intermediate stages of the process.

It is generally assumed that the presence of organic compounds does not show up in the alkalinity value. In order to investigate this point the author has tried in the present work a new way of treating the material. This consisted in using well established relationships, not varying from year to year, for calculating approximate alkalinities with the object to account for as great a part as possible of the alkalinities found by analysis. There are three such relationships: (1) that between the alkalinity and the chlorinity in oceanic water, (2) that between the concentration of calcium + strontium ions and the chlorinity in oceanic, and (3) in Baltic water. The idea of considering these relationships in discussing Baltic alkalinities is not new, but BUCH as well as WITTIG (1940) applied them to the general equations only, whereas here I have used the single alkalinity values. This procedure gives the differences between actual and calculated values increased significance.

When the alkalinities are recalculated on a kilogramme basis, the equation relating the alkalinity and the chlorinity in oceanic water becomes:—

$$\text{Alk meq/kg} = 0.120 \text{ Cl } ^0_{/00} \quad \dots (1)$$

The equation chosen for calculating the calcium concentration in oceanic water was the one used by WATTENBERG (1933):—

$$\text{Ca mg/kg} = 21.56 \text{ Cl } ^0_{/00} \text{ or } \text{Ca meq/kg} = 1.078 \text{ Cl } ^0_{/00} \quad \dots (2)$$

As to the concentration of the calcium ion in Baltic water, there are four equations valid in the separate water masses. The following three, recalculated on a meq/kg basis, are of interest in the present connexion:—

$$\text{Bottom water, Baltic} \dots \dots \text{Ca meq/kg} = 1.130 + 1.018 \text{ Cl } ^0_{/00} \quad \dots (3)$$

$$\text{Surface water, Baltic and Gulf of Finland} \dots \dots \text{Ca meq/kg} = 0.413 + 1.191 \text{ Cl } ^0_{/00} \quad \dots (4)$$

$$\text{Surface and bottom water, Gulf of Bothnia} \dots \dots \text{Ca meq/kg} = 0.095 + 1.289 \text{ Cl } ^0_{/00} \quad \dots (5)$$

These equations are founded on 40 analyses made by the author (GRIPENBERG, 1937) according to a method involving a single precipitation of the calcium ion with ammonium oxalate. The standard deviations for the three equations were found to be ± 0.030 , ± 0.025 , and ± 0.015 meq/kg respectively, the average deviation calculated on the whole material was 0.02 meq/kg or about 0.45%.

The author is not unaware of the criticism which has been raised against her method (ROBERTSON and WEBB, 1939; BARNES, 1955). ROBERTSON and

WEBB found spectrophotometrically that the precipitates were contaminated with sodium and magnesium oxalate and that, on the other hand, part of the calcium remained in solution. The errors were of the order of 2 to 3%. This does not alter the fact that the greatest deviation of any observed Ca value from the calculated relationships quoted above was 0.6% and the average deviation less than 0.5%, a circumstance which is not unimportant when judging the value of the method. It is, as a matter of fact, unessential what metals enter the precipitate, since it is the oxalate therein which is determined and not the calcium. It is the time of digestion which is all important. The accuracy thus depends upon a compensation of errors, a peculiarity which the method shares with many others. The equation for Baltic bottom water was confirmed in an extensive investigation by Hanna WITTIG (1940) who used the method with minor modifications. WITTIG found identical or almost identical equations—hers are given with one decimal place less than the author's—for the bottom water in the basins of the southern Baltic. Somewhat surprisingly the author's equation was also found valid for surface samples collected on a voyage Oslo-Kiel through the Great Belt, thus for chlorinities much higher than those occurring in the northern and central Baltic on which it was founded. This result, which reflects the manner of formation of Baltic bottom water, speaks against large systematic errors in the analyses. More important for judging the value of the method are 150 calcium and magnesium analyses recently published by KOROLEFF and FINNILÄ (1955) and by VOIPIO (1957) and founded on a completely different method. These workers for the first time used complexometric titration with Complexone III or EDTA, the di-sodium salt of ethylenediaminetetraacetic acid, in an extensive study of sea water. VOIPIO was chiefly interested in the magnesium concentration which he presented in the form of the ratio Mg/Cl. The magnesium content is found as the difference between two titrations:— in the first Mg + Ca + Sr is determined, in the second Ca + Sr. VOIPIO having kindly put his analyses at the author's disposal, it was possible to draw up the diagram (Figure 3) where all VOIPIO's and FINNILÄ's Ca + Sr analyses for the Gulf of Bothnia and the Baltic have been introduced and, in addition, the lines corresponding to the author's equations (3), (4), and (5). As to the accuracy of the complexometric Ca determination, VOIPIO (1959) states that negative errors up to 1.5% are possible. The figure shows in fact that the lines form the upper limit of the complexometric values of which about 40% lie on the lines or do not differ by more than 0.02 mg-at from these. VOIPIO's analyses include a few of water of high chlorinity from the Kattegat (Table 2). These show a very good agreement between the two methods.

Table 2

Comparison between complexometric Ca analyses and values calculated from the author's equation for Baltic bottom water

Cl	Ca mg-at/kg		Difference
	VOIPIO	GRIPENBERG	
12.92	7.10	7.14	0.04
18.57	10.01	10.02	0.01
18.80	10.08	10.13	0.05
19.19	10.29	10.33	0.04

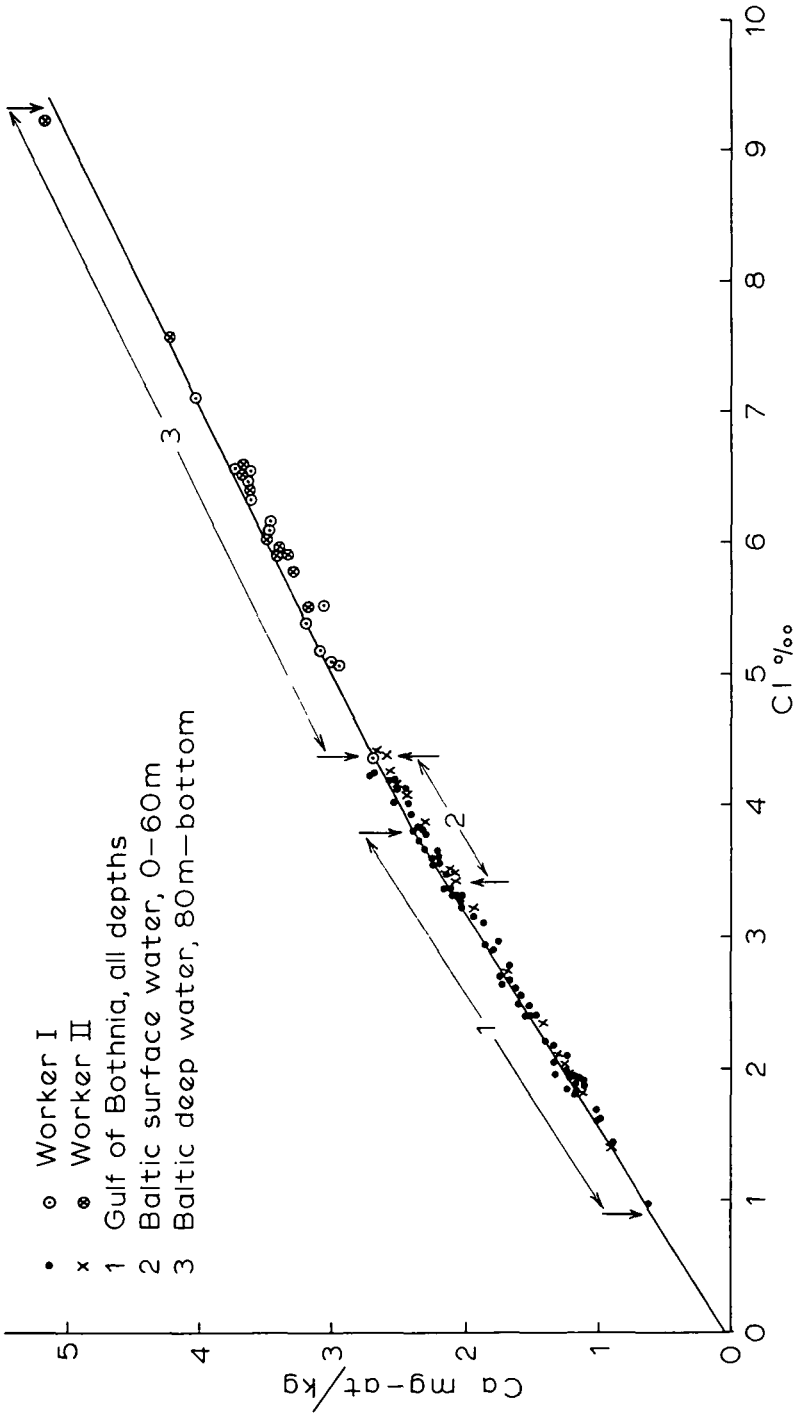


Figure 3. Comparison of the calcium analyses made by FINNILÄ and VOPIO with those of the author. The latter are given as straight lines corresponding to linear equations valid for the Gulf of Bothnia, Baltic surface water, and Baltic deep water. Arrows indicate extreme chlorinities of the water samples concerned.

The systematical differences here may be said to lie within the permissible analytical errors. This proves again that the author's equation (3) for Baltic bottom water is valid for much higher chlorinities than those for which it was calculated and still more for these. Since the standard deviations for equations (4) and (5) were smaller than for (3), the two first are probably also accurate and all three equations can safely be used for calculating approximate alkalinities in the different water masses of the Baltic.

As to the possible influence of dissolved magnesium carbonate on the alkalinity value, nothing could be said until the recent publications by VOIPIO and by FINNILÄ. According to VOIPIO the ratio of Mg to Cl is constant within a few per cent over the whole of the Baltic, the average being

$$\text{Mg mg-at/kg/Cl } ^0/_{00} = 0.275,$$

a value which lies within the narrow range of ratios valid for different parts of the oceans. There is thus no excess of magnesium in the Baltic or, in other words, in river water dissolved magnesium carbonate as a deliverer of bicarbonate ions to the Baltic, may be left out of consideration. This is, of course, not strictly true since we know that rivers do bring down Mg- and Cl-ions and the Mg-ions may derive from dissolved carbonate. But since in this case the ratio Mg/Cl in the river water, on an average, must be equal to that in the sea, the Mg-ions may have another origin. The constant ratio is perhaps a consequence of the fact that wide land areas bordering on the Baltic were covered by the sea at one time or another after the last ice age. In any case, it is safe to assume that the increased alkalinity in the Baltic is chiefly due to dissolved calcium carbonate. This has always been taken for granted and has now been confirmed by VOIPIO's and FINNILÄ's magnesium analyses. In the calculations the unknown amounts of carbonate and bicarbonate ions can be replaced by well-known Ca concentrations. No other cations need be taken into account.

The surplus alkalinity, Alk_x

An approximate alkalinity value may be computed as the sum of two parts, one derived from Atlantic water, the other equivalent to the excess of calcium, i.e., the difference between the Ca content of Baltic and oceanic water. The quantity so defined may be called *minimum alkalinity* or Alk_{min} . Combining equations (1) and (2) with (3), (4), and (5) we get the following three equations for calculating the minimum alkalinity:—

$$\text{Baltic bottom water. } \text{Alk}_{\text{min}} \text{ meq/kg} = 1.130 + 0.060 \text{ Cl } ^0/_{00} \text{ (6)}$$

$$\text{Baltic surface water } \text{Alk}_{\text{min}} \text{ meq/kg} = 0.413 + 0.232 \text{ Cl } ^0/_{00} \text{ (7)}$$

$$\text{Gulf of Bothnia, all depths . } \text{Alk}_{\text{min}} \text{ meq/kg} = 0.095 + 0.331 \text{ Cl } ^0/_{00} \text{ (8)}$$

The difference between the minimum alkalinity, which is a function of the chlorinity, and the actual alkalinity, found by analysis, will be called *surplus alkalinity* or Alk_x . In Table 1 Alk_{min} and Alk_x are found in columns 4 and 5. In Figure 2 the values of Alk_{min} are found to the left of those of Alk_{obs} . The horizontal distances between the two curves are thus equal to Alk_x . In computing Alk_{min} for the Baltic samples the surface equation (7) was used down to the salinity discontinuity at 60 m, from then on the bottom equation was applied.

Table 3

Mean values of Alk_x , the surplus alkalinity, in milliequivalents per kilogramme of sea water at the 8 stations

Gulf of Bothnia:				
	F12	F25A	F29	F64
0 m – bottom	0.072	0.066	0.064	0.060
Baltic:				
	F72A	F78B	DBS8	DBS5
0 m – 60 m	0.115	0.088	0.100	0.109
80 m – bottom	0.148	0.158	0.129	0.166

In considering the values of the surplus alkalinity one must bear in mind that all the various analytical errors enter in full into these values, though the errors may in part compensate each other. It is, therefore, not surprising that the values are uneven. Not too much importance should be attached to the single values, but we should rather pay attention to the general picture which they present. Several interesting conclusions can be drawn of which the first is that the surplus alkalinity is not a function of the chlorinity. Table 3, which gives mean values of Alk_x at the different stations, takes us a step further.

It is seen that in the Gulf of Bothnia with its homogeneous water the mean surplus alkalinity is low and almost constant with a slight decrease towards the south, whereas in the Baltic proper the values are higher and there is a distinct difference between the surface and the bottom layers. Considering now conditions at the separate stations, we see from Figure 2 that in the Gulf of Bothnia there is a more or less pronounced decrease towards the bottom starting from a small increase at 40 or 60 metres. The decrease is most marked at F64 and especially noticeable when we compare the bottom value there with those at the three other stations. Thus when proceeding from north to south and from surface to bottom, the surplus alkalinity gradually disappears. At the bottom of the water column at F64, the southernmost and deepest station, it has actually vanished and the minimum alkalinity here accounts for the whole of the alkalinity found by analysis. The small negative value of Alk_x at the bottom lies quite within the analytical error. The surplus alkalinity does not disappear without leaving some traces. In his work on the carbonic acid balance in the Baltic, BUCH (1945) calculated mean values for the 8-year period 1927–1935 partly of observed, partly of calculated data for the Finnish hydrographical stations. Among the latter were the total carbon dioxide, ΣCO_2 , the excess carbon dioxide ΔCO_2 , and the carbon dioxide tension $p \text{CO}_2$; ΣCO_2 is the sum of the carbonate ions, the bicarbonate ions, and the free dissolved carbon dioxide, ΔCO_2 the carbon dioxide present in excess of the amount the water would contain if it were in equilibrium with the atmosphere; this quantity is intended as a measure of the net CO_2 production in the sea. In Table 4 the values for ΣCO_2 , ΔCO_2 , $p \text{CO}_2$ and the O_2 percentage of saturation, are taken from BUCH's data for station F64.

We see that the decrease of the surplus alkalinity is accompanied by a small decrease of the O_2 percentage and by a steady increase in ΔCO_2 , ΣCO_2 , and $p \text{CO}_2$. The comparison of Alk_x with ΔCO_2 is particularly suggestive since both are of the same order of magnitude. The inference is that there is a connex-

Table 4

Comparison of Alk_x , the surplus alkalinity, with Buch's (1945) data for station F64

Depth	0	20	40	60	80	100	150	200	250	275 m
Alk_x	0.09	.08	.08	.08	.08	.07	.05	.05	.02	.00 meq/kg
ΔCO_2	0.00	0.1	.03	.03	.03	.03	.04	.04	.05	.06 mmol/l
ΣCO_2	1.18	1.22	1.39	1.44	1.47	1.48	1.51	1.52	1.55	1.55 mmol/l
p CO_2	3.2	4.3	5.4	5.6	5.9	5.9	6.9	7.6	8.7	8.9 atm. $\times 10^{-4}$
O_2	99	95	-	90	-	90	-	87	-	82 % saturation

Table 5

Comparison of Alk_x , surplus alkalinity, for stations F78B with Buch's (1945) data for F78

Depth	0	20	60	80	100	150	200 m	
Alk_x	0.083	.097	.086	.086	.163	.159	.150	.142 meq/kg
ΔCO_2	0.00	.00	.01	.07	.25	.24	.25	.26 mmol/l
ΣCO_2	1.36	1.43	1.48	1.54	1.81	1.84	1.87	1.87 mmol/l
p CO_2	2.8	3.4	4.5	10.5	37	36	38	38 atm. $\times 10^{-4}$
O_2	98	-	-	90 ¹⁾	-	21	20	20 % saturation

Depth	250	300	350	400	425 m
Alk_x164	.165	.153	.160	.163 meq/kg
ΔCO_226	.25	.26	.25	.25 mmol/l
ΣCO_2	1.88	1.88	1.88	1.86	1.87 mmol/l
p CO_2	39	38	38	37	37 atm. $\times 10^{-4}$
O_2	-	21	-	-	19 % saturation

1) Refers to 50 m.

ion between the surplus alkalinity and the carbonic acid constituents and that, consequently, Alk_x is organic in origin.

We cannot expect to find quantitative relationships since the data compared do not refer to the same series of observations. Nor can Alk_x be supposed to be the only organic constituent of sea water subject to oxidation.

In the Baltic proper the surplus alkalinity presents quite a different picture of which station F78B gives a characteristic example. In the surface layer down to 60 m Alk_x varies between 0.083 and 0.097 meq, in the whole of the remaining water column, from 80 to 425 m, between 0.142 and 0.165 meq/kg, thus in both water masses between narrow limits. At stations F72A and DBS8 there is a minimum at 60 m, which would perhaps have been less accentuated if at this lower limit of the surface layer an intermediate equation for the calcium content had been used. Even so, it can be maintained that in the Baltic proper the surplus alkalinity does not show any tendency to disappear; in the deep water there is, if anything, a slight increase towards the bottom. For an understanding of the special conditions in the Baltic proper we turn again to BUCH's work (1945). In Table 5 are found the same data for station F78, not far situated from F78B, as in Table 4 for F64.

We see that all quantities listed in Table 5 undergo a radical change between 60 and 80 m: Alk_x is almost doubled, ΔCO_2 and p CO_2 are more than trebled and ΣCO_2 increases by 17.5%. From 80 m to the bottom conditions remain stationary but for small fluctuations. The decisive factor is the oxygen supply.

Oxidation goes on in the surface layer as is seen from the moderately increasing values of ΔCO_2 , ΣCO_2 , and $p \text{CO}_2$. This is paralleled by a small decrease in Alk_x , illustrated more clearly, as already pointed out, at stations F72A and DBS8. At the lower limit of the surface layer the water is still saturated with oxygen to about 90%. Below 80 m, however, the water contains only about 25% of this amount and from 100 m to the bottom the saturation percentage remains at about 20%, i.e., no or only a slight further oxidation takes place. According to BUCH, conditions are practically the same within the whole of the Baltic deep-water mass. The remarkable change taking place below 60 m, notably in the oxygen content, is not due to intense oxidization at this level, but to the fact that the deep water is practically isolated from the surface layer. Organic matter accumulates in the deep and is consumed only in the measure that oxygen, brought chiefly by horizontal movements within the water mass, is available. An equilibrium has established itself characterized by practically constant concentrations of the carbonic acid constituents and oxygen. BUCH (1945, pp. 144 and 146) sums up the situation by stating that the Baltic deep water evidently contains "more oxidizable matter than there is oxygen to oxidize it", whereas in the Gulf of Bothnia there is much less organic matter and more than enough oxygen.

The surplus alkalinity fits perfectly well into the above picture and it seems to the author that there is only one possible conclusion: *the surplus alkalinity is in itself an organic constituent of sea water*. Thus, in spite of the quite different hydrographical conditions, the variations of the surplus alkalinity in the Gulf of Bothnia and in the Baltic proper have led to the same conclusion as to its character.

As was pointed out earlier and as is seen from Table 1 and Figure 2 the alkalinity decreases at the bottom of the water column at stations F25A, F29, and F64. Since WATTENBERG (1933) in his work on the solubility of calcium carbonate in sea water had shown that Atlantic water, down to 100–500 m is oversaturated with respect to CaCO_3 , and that the alkalinity decreases when carbonate is precipitated—chemically or biologically—it has been considered that precipitation or solution of calcium carbonate are the only factors which can bring about a change in the alkalinity, as expressed by the Alk/Cl value (KOCZY, 1956). Such an explanation, however, is not valid for the bottom water in the northern Baltic, BUCH (1945, p. 202) as well as the author (GRIPENBERG, 1937, p. 172) having shown that the deep water is always undersaturated with respect to calcium carbonate. The oxidation of Alk_x in water rich in oxygen offers, on the contrary, a simple explanation. If the chlorinity remains constant within a water mass, or nearly so, then the minimum alkalinity, which is a chlorinity function, also remains constant; consequently, if Alk_x diminishes, the alkalinity must diminish too. It is probable that oceanic water also has a certain surplus alkalinity, though this is more difficult to define than its Baltic counterpart, and that the small fluctuations observed in the Alk/Cl value in the water masses of the oceans at least in part should be ascribed to fluctuations in the surplus alkalinity, i.e., in the organic content of the water, the surplus alkalinity forming a part of the latter.

Though the author does not maintain that the surplus alkalinity stands for the whole of the organic matter in Baltic water, it may perhaps serve as a rough measure thereof. It has the advantage of being readily accessible to analysis.

The role played by boric acid

Though the comparison with BUCH's carbonic acid data has thus led to the conclusion that the surplus alkalinity is organic in origin, it is not necessary to assume that it consists entirely of anions of weak organic acids. When comparing the few analyses of boric acid, made in connexion with the electrometric alkalinity titrations, with the corresponding values of Alk_x it is seen that in the Bothnian surface water and in the Baltic surface and bottom water both quantities are of the same order of magnitude and in three cases (F78B, 0 m, DBS5, 0 and 105 m) even identical within the analytical errors. This suggests that there may be a connexion between the surplus alkalinity and the boric acid concentration. Now it is a well known fact, on which also the analysis for boron is founded, that boric acid easily forms complexes with organic oxy-compounds, such as carbohydrates. Acids are formed which are stronger than the simple boric acid, but are still weak acids. BUCH (1945, p. 137) concluded from the mean ratio of ΔCO_2 to ΔO_2^*) in Baltic deep water (ΔO_2 being defined as the difference between the oxygen saturation value and the actual oxygen concentration, both in mmol/l) that the dissolved organic matter consists mainly of substances having the character of carbohydrates. It is therefore possible that Alk_x is not formed directly of anions of organic acids, but rather of organic decomposition products coupled with boric acid. If this is true, the boric acid present in the water may become wholly or partly titrated already in the alkalinity analysis though it is not recognized as such, but is included in the alkalinity value. In the measure that the dissolved organic matter becomes oxidized, as in the deep water at station F64, the boric acid is gradually liberated from its organic appendage and goes back into its ordinary state. It is therefore obvious that complicated conditions may prevail near and at the equivalence point in the alkalinity titration and these conditions may vary from sample to sample, depending on the state of oxidation of the organic matter and on how much of the boric acid becomes co-titrated. The equivalence point will depend upon whether the water contains the simple boric acid, a stronger complex acid, or both. As a matter of fact, small unevennesses in the electrometrical titration curves, both before and after the equivalence point, were often observed. These were taken as technical imperfections and were levelled out in the interpolation for the equivalence point, but some of them may actually have been secondary equivalence points. The lack of adjustment of Baltic alkalinity values to a strictly linear relationship to the chlorinity may find its explanation in these circumstances and especially in the fact that the surplus alkalinity is not a chlorinity function. The boric acid analysis may be less influenced since so much mannitol is added in this analysis that the boric-acid-mannitol complex may prevail over already existing combinations.

GAST and THOMPSON (1950) have shown that the boric acid concentration of sea water increases when the water is treated with permanganate in acid solution. They present analyses of the boric acid content before and after oxidation in 32 samples from 2 stations, one in the north-east Pacific, the other in Puget Sound. The increase in the boron content varied from zero to 0.015 meq. They conclude that part of the boric acid contained in the water was combined with polyhydroxy organic matter before the oxidation and thus inaccessible to

*) The ratio is compared with the *respiratory quotient*, RQ, used in physiology.

combination with the mannitol added in the analysis. The results are given as mmols of polyhydroxy organic matter per litre (twice the amount as meq). The authors assume that the organic boric acids—like the mannitol boric acid—are much stronger than the simple boric acid and therefore titratable with sodium hydroxide in the alkalinity back titration. This results in a lower alkalinity value than would have been obtained if the water had not contained organic boric acid complexes. Such a conclusion cannot be drawn from the Baltic material. In the Baltic the organic boric acids, though stronger than the simple boric acid, must still be weak acids, or, in other words, in the electrometric back titration the equivalence point which coincides with the inflection point of the titration curve, must occur before the organic acids have been titrated. Otherwise one cannot explain that in the Gulf of Bothnia the decrease of the alkalinity in the depth—where the chlorinity is practically constant—is accompanied by a decrease of the surplus alkalinity. If the conclusion of GAST and THOMPSON were valid the opposite should be the rule. This is an important point which further work must clarify. The work of GAST and THOMPSON which has been confirmed by NOAKES and HOOD (1959), who even obtained higher organic borate values, is of utmost importance since it draws the attention of scientists to the significant connexion between the alkalinity, the organic matter, and the boric acid concentration of sea water and shows that the problem of the organic matter content can be attacked from new angles. It has an important bearing also on the conditions governing the precipitation of calcium carbonate in the sea. The notion of the surplus alkalinity in the Baltic, arrived at from an entirely different point of view, may contribute to amplify the picture.

The division of the alkalinity into two parts, the minimum and the surplus alkalinity, was originally prompted simply by a wish to separate the known from the unknown and by studying the variations of the unknown to gain some information on its nature. It is the hope of the author that the conclusions arrived at may serve as a working hypothesis for further investigations.

Summary

Sixty-five alkalinity and thirteen boric acid analyses of Baltic water are presented. A new way of treating the material is proposed founded on three well established relationships: (1) that between the alkalinity and the chlorinity in oceanic water, (2) that between the Ca concentration and the chlorinity in oceanic, and (3) in Baltic water.

A quantity called *minimum alkalinity* is defined. This is composed of two parts, one derived from the alkalinity of the oceanic fraction of the water, the other from the excess calcium, i. e., the difference between the calcium content of Baltic and oceanic water. This part is due to dissolved carbonate brought down by rivers.

Three equations, (6), (7), and (8) are computed, valid for the bottom and surface water of the Baltic proper and for water of all depths in the Gulf of Bothnia.

The difference between the alkalinity found by analysis and the minimum alkalinity is called *surplus alkalinity* or Alk_x . Alk_{min} and Alk_x are found in columns 4 and 5 of Table 1. In Figure 2 the curve for Alk_{min} lies to the left of Alk_{obs} . The horizontal differences between the two are equal to Alk_x . It is

concluded from the variations of Alk_x in the Gulf of Bothnia and in the Baltic proper compared with those of certain carbonic acid constituents, ΣCO_2 , ΔCO_2 , and $p \text{CO}_2$, as calculated by BUCH (1945), that Alk_x is in itself an organic constituent of the water. It is, however, recognized that Alk_x may not be made up directly of anions of weak organic acids, but rather of organic decomposition products forming complex anions with boric acid.

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