Excess calcium and alkalinity in the Baltic and Southern Kattegatt

Magnesium
Calcium
Alkalinity
North Sea
Baltic Sea

Magnésium
Calcium
Alcalinité
Mer du Nord
Baltique

L. Anderson, D. Dyrssen
Department of Analytical and Marine Chemistry, Chalmers University of Technology and University of Göteborg, S-41296 Göteborg, Sweden.

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ABSTRACT

Reconsideration of Kremling's data, for Baltic Sea waters together with our own data for the Southern Kattegatt and the North Sea leads to the following relations for Baltic Sea waters:

A_t (mmoles/kg) = 0.0473 Cl + 1.42,

Ca_t (g/kg) = 0.0204 Cl + 0.0225,

Mg_t (g/kg) = 0.0665 Cl + 0.0036.

The equation for calcium is based on the titration of calcium together with strontium.

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RÉSUMÉ

Apport en calcium et variations de l'alcalinité dans la Baltique et le Sud-Kattegatt

Les résultats que Kremling avait obtenus dans la Baltique ainsi que les mesures que nous avons effectuées dans le sud du Kattegatt et dans la Mer du Nord, ont servi à établir les relations suivantes pour les eaux de la Baltique :

A_t (mmoles/kg) = 0,0473 Cl + 1,42,

Ca_t (g/kg) = 0,0204 Cl + 0,0225,

Mg_t (g/kg) = 0,0665 Cl + 0,0036.

L'équation relative au calcium est basée sur une détermination de la concentration globale de calcium, incluant le strontium.

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INTRODUCTION

Kremling (1970, 1972) has shown that, while the ratios of Mg/Cl, K/Cl and SO_4/Cl have values which are close to the oceanic ratios, there is an excess of calcium and alkalinity in Baltic Sea waters. In addition, there is a slight excess of salt reflected in the Knudsen relation S = 1.805 Cl + 0.03. The simplest explanation is that the rivers entering into the Baltic contain (Ca, Mg)$(HCO_3)_2$ in the range of 0.7 mmol/l (100 mg/l), while the concentrations of other main constituents (e. g. Na^+, K^+, Cl^- and SO_4^{2-}) are lower (Dyrssen, Wedborg, 1980).

In this paper we wish to reconsider Kremling's data together with some of our own data for the Southern Kattegatt and the North Sea, and test a model of Baltic Sea waters consisting of North Sea water diluted with x mmoles Ca^{2+}, y mmoles Mg^{2+} and $2(x+y)$ mmoles HCO_3^- per kg river water.

RESIDUAL CALCIUM

Kremling (1970, 1972) summarizes his calcium (+strontium)-chlorinity data in the following equations (g/kg-°/$_{oo}$):

$Ca_t = 0.0210\ Cl + 0.0191$ (1966),

$Ca_t = 0.0216\ Cl + 0.0174$ (1967, Cl<4.5°/$_{oo}$),

$Ca_t = 0.0200\ Cl + 0.0247$ (1967, Cl>4.5°/$_{oo}$),

$Ca_t = 0.0201\ Cl + 0.0234$ (1968, Cl<4.5°/$_{oo}$),

$Ca_t = 0.0204\ Cl + 0.0218$ (1968, Cl>4.5°/$_{oo}$),

$Ca_t = 0.0219\ Cl + 0.0168$ (1969, Cl<4.5°/$_{oo}$),

$Ca_t = 0.0203\ Cl + 0.0228$ (1969, Cl>4.5°/$_{oo}$),

$Ca_t = 0.0226\ Cl + 0.0126$ (1970, Cl<4.5°/$_{oo}$),

$Ca_t = 0.0207\ Cl + 0.0199$ (1970, Cl>4.5°/$_{oo}$).

In addition, he cites the equations of Gripenberg (1937):

$Ca_t = 0.0204\ Cl + 0.0226$,

and Trzosinska (1968):

$Ca_t = 0.0204\ Cl + 0.0239$,

$Ca_t = 0.0228\ Cl + 0.0127$.

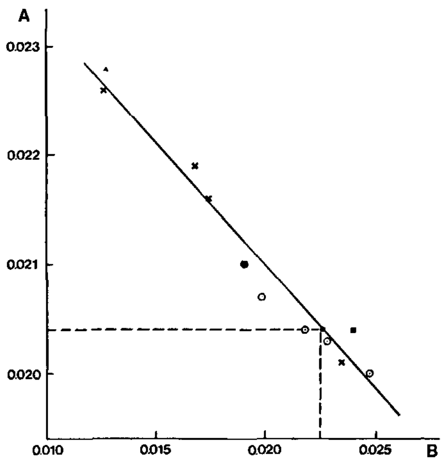

Figure 1

Covariation of the coefficients in the equation for the calcium (+strontium)-chlorinity relation: Ca_t (g/kg) = A × Cl + B. The dashed lines with A = 0.0204 and B = 0.0225 represent the best fit to North Sea waters. Crosses (Cl<4.5°/$_{oo}$) and open circles (Cl>4.5°/$_{oo}$) are data of Kremling (1970, 1972). Filled symbols are data of Gripenberg (1937) and Trzosinska (1968).

The covariation in the constants of these equations is demonstrated in Figure 1. Using A and B for the coefficients of the calcium-chlorinity ratio:

$Ca_t(g/kg) = A \times Cl + B$,

the relation between A and B is given by:

$A = -0.227\ B + 0.0255$.

The Ca_t/Cl ratio for North Atlantic waters is most likely in the range 0.021 47 (Riley, Tongudai, 1967) to 0.021 66 (Kremling, 1972), if strontium is titrated together with calcium. A and B can be fitted to the oceanic ratio by using the following equations:

$Ca_t = Cl(-0.227\ B + 0.0255) + B$,

$Ca_t/Cl = 0.02156$,

$Cl = 19.374$.

The equations lead to the following relation, which should be valid for the Danish Sounds as well as the Baltic Sea:

$Ca_t(g/kg) = 0.0204\ Cl + 0.0225$.

This equation is very close to the formula presented by Gripenberg (1937). The residual calcium corresponds to 0.56 mmoles/kg. Millero (1978) obtained 0.0210 ± 0.0022 (g/kg).

A similar covariation can be seen from Kremling's salinity-chlorinity relationships. In fact the equation

$S = (35 - B)\ Cl/19.374 + B°/_{oo}$,

fits to both S = 1.80655 Cl (B = 0), and the Knudsen relation S = 1.805 Cl + 0.03 as well as other equations with other values of the residual salinity B.

RESIDUAL ALKALINITY

Kemling (1970, 1972) has determined the alkalinity of Baltic Sea waters in the spring and fall of 1967-1970. He presents the data in mmoles/l, but since Millero and Kremling (1976) have determined the densities of the same samples, it is possible to recalculate the data in mmoles/kg. Some of our data for the Southern Kattegatt are given in Table 1, and for North Sea waters in Table 2. From the data in Table 1, we may establish an alkalinity value of 2.333 mmoles/kg for Kattegatt bottom water at S = 35°/$_{oo}$. Furthermore, it is obvious that the specific alkalinities of the Baltic Sea waters are considerably

Table 1

Alkalinity data for the Southern Kattegatt (Latitude 56°38′N) on March 14 (stations 1-5) and 15 (stations 6-10) 1978.

Stations Nr.	Long. E	Depth (m)	Cl (%)	A_t (mmol/kg)	A_t/Cl (mmol/kg/°/$_{oo}$)
1	10°34′	1	11.84	1.945	0.1643
		8	17.55	2.307	0.1315
2	10°47′	1	12.66	1.894	0.1496
		6	15.83	2.117	0.1337
3	11°00′	1	11.52	1.919	0.1666
		10	17.43	2.282	0.1309
4	11°13′	4	11.16	1.927	0.1727
		14	18.05	2.297	0.1273
5	11°26′	4	11.05	1.830	0.1656
		14	13.89	2.074	0.1493
6	11°38′	5	11.24	1.957	0.1741
		25	18.85	2.307	0.1224
7	11°51′	5	12.26	1.917	0.1564
		20	18.32	2.299	0.1255
8	12°04′	5	11.40	1.927	0.1690
		20	18.35	2.187	0.1192
9	12°17′	5	12.75	1.948	0.1528
		20	19.11	2.316	0.1212
10	12°30′	3	11.96	1.871	0.1564
		19	18.02	2.203	0.1223

Table 2

Data from station M6 (58°10′N, 9°30′E) in the Skagerrak part of the North Sea. Sampled and analyzed on board R/V Argos 1976-04-07.

Depth (m)	Cl (°/₀₀)	A_t (mmol/kg)	C_t (mmol/kg)	A_t/Cl (mmol/kg/°/₀₀)
0	15.452	2.1171	1.9431	0.1370
5	15.458	2.1159	1.9448	0.1369
10	18.136	2.2352	2.0294	0.1232
15	18.954	2.2888	2.0897	0.1208
20	19.008	2.2923	2.0917	0.1206
30	19.116	2.2969	2.0934	0.1202
40	19.220	2.2884	2.0828	0.1191
50	19.284	2.2941	2.0826	0.1190
75	19.349	2.3076	2.0938	0.1193
100	19.373	2.3062	2.0980	0.1190
125	19.377	2.3151	2.1095	0.1195
150	19.379	2.3044	2.0969	0.1189
200	19.409	2.3470	2.1394	0.1209
300	19.432	2.3031	2.1076	0.1185
400	19.449	2.2931	2.1045	0.1179
500	19.441	2.3110	2.1167	0.1189
600	19.460	2.3009	2.0941	0.1182

larger than $A_t/Cl = 0.12$ mmoles/kg per °/₀₀. The scatter in the alkalinity data is due in part to the analytical error, and mostly to the varying alkalinity of the river waters together with incomplete mixing. One way of treating Kremling's data for chlorinities between 4 and 14°/₀₀ and stations F1 to F8 is to minimize the error square sum

$$[A_t(\text{measured}) - A_t(\text{calculated})]^2,$$

where

$$A_t\,(\text{calculated}) = \frac{2.333 - B}{19.374}\,Cl + B.$$

In this way, the following residual alkalinities (B) were obtained:

Period	Residual alkalinity (=B) (mmoles/kg)
Spring 1967	1.46
Fall 1967	1.47
Spring 1968	1.45
Spring 1969	1.47
Fall 1969	1.40
Spring 1970	1.38
Fall 1970	1.28
Mean value	1.416

Thus this residual alkalinity will correspond to 0.71 mmoles/kg of calcium and magnesium ions. Since the residual calcium obtained above was 0.56 mmoles/kg, the magnesium would be 0.15 mmoles/kg or 3.6 mg/kg. Millero (1978) obtained 3.8 ± 2.2 mg/kg.
This residual magnesium is only about one per cent of the magnesium concentration of most Baltic Sea waters, and therefore barely discernible considering the analytical error in the determination of magnesium.

North of the Danish sounds measurements in the Southern Kattegatt (along lat. 56°38′N) show a somewhat lower residual alkalinity (1.28 mmoles/kg). This is most likely due to the fact that Swedish rivers entering the Skagerrak and Kattegatt part of the North Sea have a lower alkalinity. This is also true for the Norwegian rivers (cf. Danielsson, Dyrssen, 1975). There is, however, a certain decrease, in the residual alkalinity in the 1967-1970 data.

CONCLUSIONS

The river input of (Ca, Mg) $(HCO_3)_2$ into Baltic Sea waters will correspond to approximately 1.42 mmoles/kg of HCO_3^-, 0.56 mmoles/kg of calcium and 0.15 mmoles/kg of magnesium. This will lead to the following relations:

A_t (mmoles/kg) = 0.0473 Cl + 1.42,

Ca_t (g/kg) = 0.0204 Cl + 0.0225,

Mg_t (g/kg) = 0.0665 Cl + 0.0036.

The excess alkalinity of the Baltic current can be traced all the way along the coasts of Sweden and Norway, as can be seen from Table 2 and Figure 2. The lower specific alkalinity (A_t/Cl) of the North Sea water (the mean value from Table 2 is 0.1193 mmoles/kg per °/₀₀) is mostly likely due to the formation of zooplankton shells and nitrate (cf. Dyrssen, 1977).

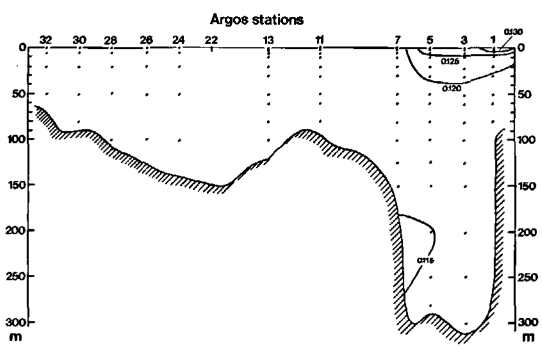

Figure 2

The Joint North Sea Data Acquisition Program 1976 (Jonsdap 76) section Ar1-Ar15, Ar22-Ar32 from Egeröy (58°26′N) via Fladen Ground (the Flex Box) to Aberdeen 1976-03-23 to 1976-03-25. The isolines represent the A_t/Cl values of 0.115, 0.120, 0.125 and 0.130 mmoles/kg per °/₀₀. The points represent data available at our department. They show that the specific alkalinity of the North Sea is quite uniform. The station numbers and positions are:

Station	Position		Station	Position	
Ar 1	58°26′N	5°45′E	Ar 22	58°26′N	0°40′
3	58°26′N	5°14′	24	58°26′N	0°00′
5	58°26′N	4°37′	26	58°09′	0°20′W
7	58°26′N	4°00′	28	57°54′	0°43′
11	58°26′N	2°45′	30	57°41′	1°05′
13	58°26′N	1°44′30″	32	57°30′	2°24′

REFERENCES

Danielsson L.-G., Dyrssen D., 1975. Chemical investigation of Idefjord on July 24, 1975. Report on the chemistry of sea water XVI, Department of analytical chemistry, Univ. Göteborg.

Dyrssen D., 1977. The chemistry of plankton production and decomposition in sea-water, in: *Oceanic sound scattering prediction*, edited by N. R. Andersen and B. J. Zahuranec, Plenum Press, 1977, 65-84.

Dyrssen D., Wedborg M., 1980. Major and minor elements, chemical speciation in estuarine waters. Ch. 3, in: *Chemistry and biogeochemistry of estuaries*, edited by E. Olausson and I. Cato, John Wiley.

Gripenberg S., 1937. The calcium content of Baltic water, *J. Cons. Int. Explor. Mer*, **12**, 293-304.

Kremling K., 1970. Untersuchungen über die chemische Zusammensetzung des Meerwassers aus der Ostsee, II. Früjahr 1967-Früjahr 1968, *Kiel. Meeresforsch.*, **26**, 1-20.

Kremling K., 1972. Untersuchungen über die chemische Zusammensetzung des Meerwassers aus der Ostsee, III. Früjahr 1969-Herbst 1970, *Kiel. Meeresforsch.*, **28**, 99-118.

Millero F. J., 1978. The physical chemistry of Baltic Sea waters, *Thalassia Jugosl.*, **14**, 1-46.

Millero F. J., Kremling K., 1976. The densities of Baltic Sea waters, *Deep-Sea Res.*, **23**, 1129-1138.

Riley J. P., Tongudai M., 1967. The major cation chlorinity ratios in sea water, *Chem. Geol.*, **2**, 263-269.

Trzosinska A., 1968. Distribution of the calcium and magnesium ion content in the Baltic water, VI. Conference of the Baltic oceanographers, Sopot, June 6-8, 1968.