# Some peculiar features of the hydrochemical regime and the fauna of mesohaline waters

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### Abstract

The information available reveals pronounced changes in the ion ratio when marine and fresh waters are mixed. The critical salinity has been shown to be about  $5^{0}/_{00}$  in the Kara, White, Baltic, Azov, Black and, probably, Caspian Seas, and British Columbia. Corresponding results were obtained in experimental mixings of White Sea waters with a variety of fresh waters. A close connection is suggested between mixed water hydrochemistry and the existence of an eco-physiological barrier. This barrier divides, at salinities of 5 to  $8^{0}/_{00}$ , the two basic types of aquatic animals into marine and freshwater representatives.

### Introduction

The processes in the mixing zone of the sea and fresh waters became the object of systematic studies only during the last few decades. For a long time, brackish waters were outside the sphere of interest of both limnology and oceanology.

The pioneers in the study of such intermediate habitats between ocean and fresh waters (mesohaline zone) were biologists classifying mesohaline waters by means of salinity and fauna and flora characteristics. These studies have been reviewed by DAHL (1956), REMANE (1958) and SEGERSTEALE (1959). At the international symposium on the classification of mesohaline waters in Venice, Italy, a system was suggested which had been worked out mainly on the grounds of information obtained in the Baltic Sea. This system represents an extention of the systems previously proposed by REDEKE (1933) and VÄLIKAN-GAS (1933).

We have reported (KHLEBOVICH, 1962) a peculiar feature characteristic of the majority of classification systems: in different systems worked out for the mesohaline waters of the Kolsky gulf and the Baltie Sea, as well as for the estuaries of England, France, the Adriatic Seas, and South Africa, there exists a border line between different faunas at a salinity of about 5 to  $8^{0}/_{00}$  (in the Venice system  $5^{0}/_{00}$  divides mesohaline and oligonaline zones). It is important to note that mesohaline forms are mainly representative of the marine fauna, and oligohaline forms of the freshwater fauna. The result is the great biological significance of the narrow salinity range of 5 to  $8^{\circ}/_{00}$ , a rather accurate barrier, dividing the marine and freshwater faunas. It is further necessary to note that the concept of the peculiar biological significance of the 5 to  $8^{0}/_{00}$  salinity range has recently acquired new impetus (KHLEBOVICH, 1965, 1966).

# Results

In the light of this situation it seemed advisable to study details of physico-chemical conditions in relation to the above-mentioned biological law. We had, naturally, to proceed from the classical idea of permanent ion relations with a prevalence of univalent ions in sea water, and of an extreme qualitative diversity of fresh waters, where bivalent ions usually play the main role. Since mixohaline waters are the result of mixing of sea and fresh waters, the ratio of the salts dissolved in them must change accordingly and the hydro-chemical characteristics depend on the salinity. The question is: at what salinity does the Knudsen rule of the constant ion ratio of the sea water become inapplicable? Recent scientific information seems to provide an answer to this question.



Fig. 1. Relative calcium content as a function of salinity at various localities. 1 near Oslo, 2 Kiel-Bay, 3 Bornholm Deep, 4 east coast of the Baltic Sea, 5 Kiel Inlet, 6 Arkona Deep, 7 east coast of the Baltic Sea, 8 estuary of the Schwentine River, 9 estuary of the Schwentine River. (Based on data by WITTIG, 1940)

WITTIG (1940) determined the relative calcium content in water samples of different salinities taken at various points of the Norwegian and Baltic Seas. Based on WITTIG's data, we constructed the graph illustrated in Fig. 1. It demonstrates a distinct relative increase of calcium at salinities below  $5^{\circ}/_{00}$  and the practical constancy of its ratio at higher salinities.

Based on detailed hydrochemical analyses of 97 water samples of different salinities from the Kara Sea, LOBZA (1945) presented new information on ion ratios, indicating a pronounced change in the main hydrochemical characteristics of salinities below  $4^{0}/_{00}$ . A graph constructed from data published by KIRSOH (1956) reveals sudden changes of the important hydrochemical characteristics of waters near the Bute and Knight inlets (British Columbia) between 4 and  $7^{0}/_{00}$  (Fig. 2). In a recent series of determinations regarding the hydrochemistry of estuarine waters of the Black Sea, a sudden change of the ion ratio was noted at salinities of about  $3^{0}/_{00}$ , and marked divergencies from the normal chlorine coefficient were already recorded at a salinity of  $5^{0}/_{00}$  (ALMAZOV, 1962; ALMAZOV and DENISOVA, 1955; ALMAZOV et al., 1959). The same situation is typical of the waters of the Azov Sea.



Fig. 2. Relative increase of the ion ratios K:Na and Ca:Na in waters of different salinities in Bute and Knight Inlets, British Columbia. Ordinate: Ion ratio increase above 100% (normal sea water). (Based on data by KIRSOH, 1956)



Fig. 3. Correlation between salinity and chlorinity in the Azov Sea. Hatched: "mixing water zone". (After TSURIKOVA and SHULGINA, 1964)

Thus, TSURIKOVA (1962) observed a lability of the carbonate-calcium system in Taganrog inlet water at a chlorine content of less than  $4^{9}/_{00}$  which is equivalent to a salinity of about  $7^{0}/_{00}$ . According to TSURIKOVA and SHULGINA (1964), the relation between ion ratio and salinity in water of the Azov Sea shows a marked discontinuity at  $2^{0}/_{00}$ , where "the mixing zone of waters" begins at a salinity of about 5 to  $6^{0}/_{00}$  (Fig. 3); the standard correlation between electroconductivity and salinity becomes inapplicable at salinities below  $5.5^{0}/_{00}$ . TSURIKOVA and TSURIKOV (1966) noted that,

at chlorine contents lower and higher than  $2^{0}/_{00}$ , which is equivalent to a salinity of about  $4^{0}/_{00}$ , different formulae of carbonate-calcium calculations should be applied.

The most interesting data of VINETSKAVA (1959) on the correlation between flow magnitude of the river Ural and salinity of the eastern part of the North Caspian Sea (Fig. 4) may be interpreted along similar



Fig. 4. Ural River flow and salinity of the eastern part of the Northern Caspian Sea in August. (After VINETSKAYA, 1959)

lines. The sharp bend at  $70'_{00}$  salinity in VINETSKAYA's graph can be explained by the fact that, below this salinity, processes connected with the change in ion ratios take place and, possibly, by removal of certain ions from the solution.

We have studied (KHLEBOVICH and NIKULICHEVA, 1966) the calcium-chlorine ratio in the estuary of the river Keret (Kandalaksha bay of the White Sea). In one instance, at high tide, during a very dense isohaline distribution, a salinity gradient from fresh water to  $14.4^{\circ}/_{00}$  occurred over a distance of not more than 100 m. It is worth noticing that, in this case (Fig. 5a), the changes under study did not differ essentially from those taking place, according to WITTIG (1940), over hundreds of kilometres (from Oslo to the estuary of the Schwentine; Fig. 1).

An even clearer picture than that resulting from our field work on the relation between ion ratio and salinity, was obtained in 3 experiments. In the first experiment, the Ca/Cl ratio was analysed in vessels containing White Sea water diluted to various salinities with River Keret water, after defined periods (7 to 10 days) (Fig. 5b). In the second experiment, White Sea water was diluted with water from the Krivoye lake (located near the White Sea Biological Station of the Zoological Institute) previously saturated with calcium carbonate (Fig. 5c). Finally, in the third experiment, the sea water was diluted with distilled water (Fig. 5d). No changes of the Ca/Cl ratios were noted, demonstrating that the cause of ion ratio changes is associated primarily with mixing of waters of different hydrochemical properties and cannot be explained by a mere change of ion strength.

The information presented shows that many hydrochemical indexes change sharply at salinities of about 4 to  $7^{0}/_{00}$  in the basins of the Kara, White, Baltic, Black, Azov and, probably, Caspian Seas, and



Fig. 5 a—d. Changes in the ratio Ca:Cl as a function of the degree of dilution of the White Sea water; a in the Keret River estuary; b artificial dilution with Keret water in the laboratory; c artificial dilution with Lake Krivoye water saturated with Calcium carbonate; d artificial dilution with distilled water

in the estuaries of British Columbia, which are quite different and located far apart from each other.

Taking into consideration the fact that the ion ratio characteristics of different waters are, in some cases, a determinant ecological factor (BEKLEMI-SCHEW and BASKINA, 1933), we have every reason to consider the pronounced changes of hydrochemical characteristics at a salinity of about  $5^{0}/_{00}$  to be the principal cause for the existence of an eco-physiological barrier (KHLEBOVICH, 1962, 1965) which divides marine and limnic fauna representatives.

## Summary

1. There is considerable evidence suggesting that a salinity of about  $5^{0}/_{00}$  represents a zone of pronounced changes in important hydrochemical properties in all mixohaline mesohaline waters.

2. This hydrochemical peculiarity explains the existence of an eco-physiological barrier, dividing the

2 basic types of the aquatic fauna — marine and limnic — both in regard to physiological and historical aspects.

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