

# The Chemical Properties of the Waters in the Krka River Estuary (the Central Part of the Eastern Adriatic) with particular Reference to Water Pollution

by

M. BULJAN, L. STOJANOSKI, and I. VUKADIN

*Institute of Oceanography and Fisheries (Split)*

## Abstract

The results are summarily presented of chemical analyses of the waters belonging to the Krka River and the sea into which the river discharges. The fluoride content in these waters has been analyzed for the first time, and the F/Cl ratio has been discussed. The quantities of nutrient salts found in these waters and the oxygen presence in them are also shown. Conclusions are drawn with regard to the degree of water eutrophization.

## Résumé

On a donné une revue des analyses chimiques des eaux de l'aire investiguée avec une vue spéciale sur le contenu de fluorure (pour la première fois), des sels nutritifs (Si-SiO<sub>2</sub>; N-NO<sub>3</sub>; N-NH<sub>4</sub>; P-PO<sub>4</sub>; P-tot) et de relations de l'oxygène (O<sub>2</sub>, O<sub>2</sub> %). Les conclusions sur le degré d'eutrophisation des eaux en 1973/74 sont données.

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By taking into consideration the extent of pollution of both the water of the Krka River and the sea water in the port of Šibenik, the investigations, carried out from 1973 through 1974, were performed at two stations off the Krka River estuary (the outer stations), and at six stations in the estuary area (the inner stations).

**Fluorides (F<sup>-</sup>).** Their quantities range between 1488 µg/l in the high salinity sea water, and 68 µg/l in brackish water. The highest values in the column are situated deeper than the minimum values what can be explained by a constant, highly developed salinity gradient in the deeper layers of the waters in the estuary area, and by the fact that fluoride belongs to thalassophyle elements. There is an evident decrease of the values of fluoride content when starting from the sea and proceeding up the river (surface waters). The mean value amounted to 1438 ± 88 and 1441 ± 64 µg/l F respectively in the sea water column at the two outer stations located near Šibenik. The mean values found in the Brač Sound (30 Nm SE of Šibenik) amounted to 1428 µg/l F (at a depth of 33 metres) and 1415 µg/l F in the Bay of Kaštela (at a depth of 38 metres). The values of the F/Cl ratio (annual means) decrease when starting from the outer stations and proceeding up the river. The geochemical phenomenon can be explained by two possibilities, the first being the rain water which, comes into contact with the soil, carrying more chlorides than fluorides, as compared with sea water, into the waters of the River Krka. The other possibility consists in settling of F<sup>-</sup> from the sea water to the bottom in the estuary area. The first possibility should be eli-

minated as a result of our data covering the  $\text{Cl}^-$  quantities contained in the waters of the Yugoslav rivers Krka and Jadro (amounting to about  $16000 \mu\text{g/l Cl}$ ) as also the F content found in the waters of the River Jadro (amounting to from  $320$  to  $450 \mu\text{g/l F}$ ) and the there from obtained ratio  $\text{F}^-/\text{Cl}^- =$  from  $2$  to  $3 \times 10^{-2}$ . The conclusion drawn in this connexion is that F precipitation occurs in the estuary water, entering a compound, probably with  $\text{Ca}^{2+}$ .

The mean values of the  $\text{F}^-/\text{Cl}^-$  ratio in the area under investigation (the outer stations), amounting to  $6,82 \times 10^{-5}$ , do not practically differ from the ratio found in the sea water of Brač Sound (off Split) :  $6,86 \times 10^{-5}$  or from those found in the Bay of Kaštela :  $6,85 \times 10^{-5}$ . The conclusion drawn from the quoted data is that the sea water in the Šibenik port is not polluted with fluorides from the waste waters of the aluminium plant in the area.

**Nutrients salts.** The quantities of silicates ( $\text{SiO}_2 - \text{Si}$ ) recorded at the outer stations ranged between  $5,28$  and  $8,39 \mu\text{g at/l}$ , while those found in the waters of the inner stations were as high as  $60 \mu\text{g at/l Si}$ . The surface layers at the inner stations (low salinity) are about four times richer in silicates than the bottom layers (high salinity). The nitrite content ( $\text{N-NO}_2$ ) of waters is lower than  $0,054 \mu\text{g at/l}$  at the outer stations, while it rises up to  $1,90 \mu\text{g at/l N}$  at the inner stations. The range of ammonia content ( $\text{NH}_4\text{-N}$ ) was rather limited, i.e. between  $0,72$  and  $1,37 \mu\text{g at/l}$  at the outer stations, and up to  $3,04 \mu\text{g at/l N}$ . There were no developed gradients of  $\text{NH}_4^+$  salts either regarding the depth or regarding the horizontal intervals. High values of negative gradient in function of the depth were shown by the nitrates ( $\text{N-NO}_3$ ), but only in the river waters. The values recorded in the surface layer amounted  $\mu\text{p}$  to  $48,0 \mu\text{g/at N/l}$ ; however, the said values dropped to  $1/10$  or even  $1/100$  in the deeper layers, and were usually smaller than  $1,1 \mu\text{g at N/l}$  in the waters of the outer stations.

**Phosphates ( $\text{PO}_4\text{-P}$ ).** The mean values ranged between  $0,047$  and  $0,057 \mu\text{g at P/l}$  at the outer stations, while they were  $0,072$  (P-1),  $0,164$  (P-2),  $0,205$  (P-3),  $0,106$  (P-8),  $0,52$  (P-10) and  $0,024$  (P-14)  $\mu\text{g at P/l}$  at the inner stations. The pH and alkalinity data are also available.

**Oxygen ( $\text{O}_2$ ).** In the waters of up-river stations (P-10), P-14), the occurrence of "old water" has been recorded in winter. The decrease in the oxygen content found in the deeper layers of the inner stations during the period between June and November may be an indication that the process of eutrophization of waters has started. Oxygen saturation ( $\text{O}_2 \%$ ) shows that the sea water is influenced by various wastes coming from the urban agglomeration- the Šibenik city area. The changes, however, are not yet alarming.

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## Discussion

1. You estimated the precipitation of calcium fluoride. Can you tell me pH and calcium content of the river water? (R. FUKAI, Monaco).

*Answer :*

1. pH of river water is around  $7.8-8.0$  and calcium was not measured, but rather high content.