# DISTRIBUTION OF CD, PB, CU AND ZN IN CARBONATE SEDIMENTS FROM THE KRKA RIVER ESTUARY, CROATIA

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We studied distribution of trace metals (Cd, Pb, Cu and Zn) as well as some sediment components (carbonates, organic matter i.e. loss on ignition - LOI, Fe and Mn) in oxic carbonate sediments from the Krka estuary. By applied chemical extraction technique (somewhat modified procedure of TESSIER *et al.*, 1979), it is possible to distinguish : exchangeable cations (F1), carbonates (F2), hydrous oxides of Fe and Mn (F3), organic matter (F4) and residual (F5). Although carbonates are regarded rather as trace metal diluters in sediments than as their collectors, selective chemical extraction procedures are mainly designated to differentiate also the carbonate fraction between other fractions (KERSTEN AND FÖRSTNER, 1990). High metal concen-tration in this fraction is often regarded as a pollution indicator, i.e. that fraction represent metals desorbed from other substrates (like Fe and Mn hydrous oxides and organic matter). This indeed seems to be the case for polluted estuaries with prevailing non-carbonate sediments. The Krka river estuary is a non-polluted estuary with low total metal input and very low sedimentation rates (average 0.12 mm/y in the upper part, negligible in the seaward part of the estuary, PROHIC and JURACIC, 1989). Previous study of the carbonate sediments from the Krka estuary, by PROHIC and KNIEWALD (1987), showed the high percentage of some trace metals (Mn, Cu, Pb and Zn) in this fraction, despite the low metal levels in the majority of analyzed samples. Procedure was performed on grain size fractions: 300-150 , 150-61 and 61-5 µm. Trace metals were determined by differential pulse anodic stripping voltametry (DPASV). Trace metal concen-trations were found as Cd 0.156-0.399, Pb 17.3-118.6, Cu 19.1-52.1 and Zn 66.2-168.1 µg/g dry wt., in the smallest size fraction, along the estuary (sampling sites shown in Fig. 1). Distribution of trace metals differed for different size fractions. Generally, there was no relation between metals concentrations in fractions F2, F3 and F4 and the concentrations of sediment components ($CaCO_3$, organic matter, Fe and Mn. Seaward, total trace metal concentrations and carbonates increased while organic matter and Fe decreased (also did Mn, being highest at site E-4). The highest metal concentrations were obtained in F2 (Pb in 61-5 µm and Cd and Zn in 300-150 µm size fraction) and in F3 (Cu, Zn and Cd in 61-5 µm). The concentrations in other fractions were low (Fig. 2). It seems that carbonates can not be regarded exclusivly as a trace metal diluter in the actual carbonate sediments present in the Krka river estuary.

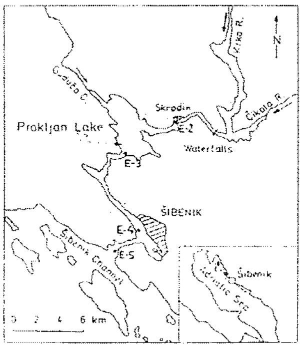


Fig. 1. The study area with the sampling sites

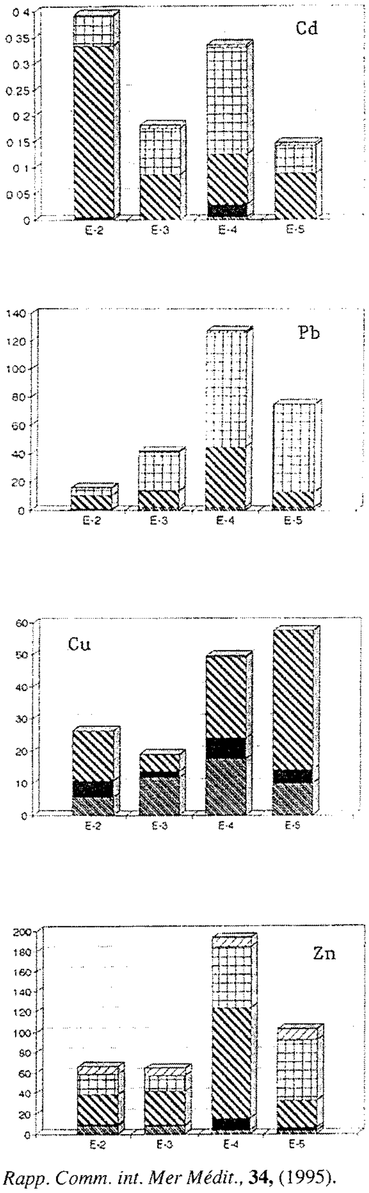


Fig. 2.. Concentrations, at four sampling sites, of trace metals (Cd, Pb, Cu and Zn) in chemical fractions of sediments for grain size fractions 61-5 µm (µg/g dry wt.).

F1
F2
F3
F4
F5

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# DISTRIBUTION OF PHOTOSYNTHETIC PIGMENTS IN THE PLUME OF THE RHONE RIVER

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Chlorophyll and carotenoid pigments are useful biomarker compounds for studying various biological processes in the marine environment. They proved to be especially helpful for providing additional information about the chemotaxonomic composition of phytoplankton as well as about formation and degradation of the phytoplankton biomass (BARLOW *et al.*, 1993). However, as opposed to a number of reports on phytoplankton dynamics in oceans by using pigments as biomarkers there seem to have been only limited number of such studies in estuarine, coastal and shelf areas (DENANT *et al.*, 1991). In such areas, additional nutrient inputs by rivers were shown to have a strong impact on phytoplankton dynamics resulting often in an enhanced standing stock of phytobiomass. The aim of this paper is to investigate the build-up of the phytoplankton biomass in the freshwater plume of the Rhone River (France). Chloro-phyll and carotenoid pigments were deter-mined according to a modified HPLC method by Mantoura and Llewellyn (BARLOW *et al.*, 1993). Briefly, water samples (2 L) were filtered through 47 mm Whatman GF/F filters and immediately frozen until analysed. Frozen filters were extracted in 4 mL 90% acetone and analysed using a gradient reversed-phase HPLC system equipped with both spectrophotometric and spectrofluorimetric detectors and dual channel data collection and integration. Chlorophylls and carotenoids were detected by absorbance at 440 nm while detection of phaeopigments was performed with a fluorescence detector using an excitation wavelength of 420 nm and emission at 672 nm. Sampling was performed in the framework of a Lagrangian experiment, aiming at studying the development of organic matter in the Rhone estuary, between 11th and 21st November 1993 (Fig. 1). Water samples for pigment analyses were collected at four different depths in the top 10 m of the water column. The experiment was undertaken on four different days, between $8^{00}$ a.m and $17^{00}$ p.m. in exact time intervals of 60-120 minutes (stations A-F). Concentrations of photosynthetic pigments in the Rhone estuary during the experiment showed a strong spatial and temporal variability (790-10800 ng/l of Chl *a*). Signatures of phytoplankton composition indicated that diatoms were the most abundant class as reflected by a pronounced predominance of fucoxanthin (fuc) over other accessory pigments (Fig. 2). Low concentrations of 19'-hexanoyloxy-fucoxanthin (hex) and chlorophyll b (Chl *b*) detected in the samples suggested a rather low contribution of Prymnesiophytes and green algae to the total phytobiomass. Moreover, comparatively low concentrations of phaeophorbides and phaeophytins (< 250 ng/l) were indicative of the freshly formed phytoplankton biomass, still mainly unaltered by grazing or other degradation processes. Distribution of photosynthetic pigments on vertical profiles in the freshwater plume of the Rhone estuary (Fig. 2) revealed a very dynamic behaviour of the phytobiomass as a consequence of the strong response to the input of riverborne nutrients, in particular nitrate. However, the concentration maxima of photosynthetic pigments were not observed at the surface, characterised by the lowest salinities and consequently the highest nitrate concentrations, but in the subsurface layer (1.5-3 m) characterised by salinities between 30-35‰ and much lower nitrate levels. This suggested that phytoplankton biomass was predominately of marine origin. Thus, the salinity range below 25‰ was probably the limiting factor which precluded a stronger build-up of marine diatoms in the uppermost layer. The diatom peaks observed on the vertical profiles can be interpreted as a compromise between the nutrient supply from the top of the water column and salinity tolerance of marine phytoplankton. The profiles similar to those presented in Fig. 2 were observed only during relatively calm weather conditions which allow the system to maintain stratification over the time periods required for a build-up of the phytobiomass.

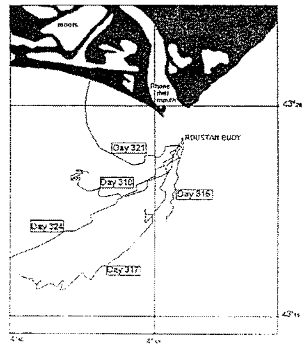


Fig. 1. Map of the Rhone estuary with indicated trajectories followed during sampling on 5 different days.

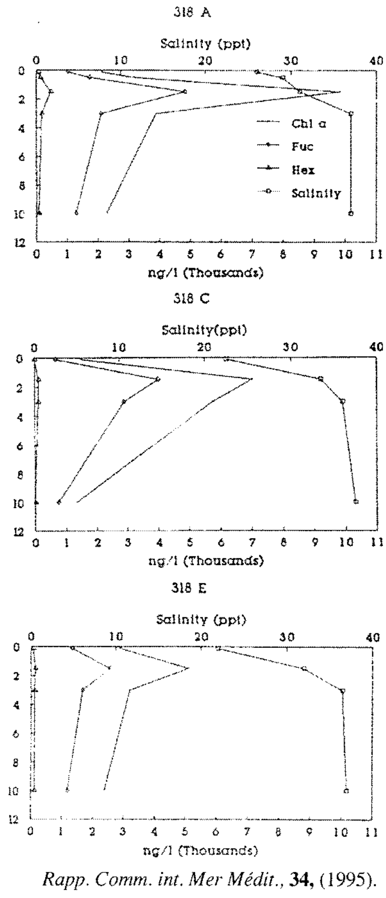


Fig. 2. Vertical profiles of chl *a* and two accessory pigments in the Rhone estuary (Day 318 see Fig. 1)

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