Calcium in sediments of the transitional river-lagoon-marine system as indicator of different biogeochemical accumulation areas

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Introduction: Calcium (Ca) plays an essential role in the formation of aquatic sediments and biogeochemical exchange processes. Yet, Ca participation in the complex processes is not substantive. Therefore, additional knowledge on Ca position with regard to other chemical elements as well as possible inter-relations with them is of major importance. Current study provides new scientific data on the amount of 27 chemical elements in different sedimentary environments, represented by 190 km long transitional aquatic chain from the Nemunas River delta to the deep-water areas of the Lithuanian part of the Baltic Sea. Main aims of the study focused on the analysis of Ca amount variations including its inter-element correlations.

Methods: Nearly one hundred surface sediment samples were collected in Nemunas River delta (n=12; average depth - 6m), freshwater Curonian Lagoon (11; 3m), heavily modified water body - Klaipėda Strait (24; 12m) and Lithuanian marine area of the Baltic Sea (49; 55m). 25 sediment samples from the marine area collected at the depths up to 53 meters (average depth of the whole Baltic Sea), other 24 samples at the depths from 54 to 120 meters. Collected samples analyzed for grain size distribution, identifying the amount of < 0.063 mm fraction (F-gs) and the amount of organic matter, expressed by the loss of ignition (LOI). Energy dispersive X-ray fluorescence spectrometer Xepos (Kleve, Germany) was used to determine contents of calcium (Ca), other major (Al, Fe, K, Mg, Mn, Na, Si, Ti) and trace (As, Co, Cr, Cu, Mo, Ni, Pb, Rb, Sr, Th, V, U, Zn) elements, basic components of marine waters (Cl, S, P, Br). Variations of all the variables evaluated using non-parametric statistic tests.

Results: Distribution of Ca along with three other most abundant metals in the Earth's crust (Al, Fe, Mg) [1], some characteristic indices of marine waters (Cl, S, P and Pb) as well as chosen sedimentation conditions indicators (F-gs, LOI) presented in Figure 1. Results of the Spearman rank correlation test presented as a sequence of significant *p* values (<0.01), arranged in the order of Ca and other variables relationship strength decrease (Table 1).

Discussion: Although Ca known to be the third most abundant metal in the Earth's crust behind Al and Fe [1], current study indicates, that in the sediments of Nemunas River delta it is the second abundant after Al, while in the lagoon and strait sediment Ca occupies dominant position (Fig.1). Distribution patterns of Ca changes in the marine area up to 53 m (Al>Fe>Ca>Mg), while in the deep-water zones it occupies fourth position after Al, Fe and Mg.

Upon the changes of sedimentary environments, specific links of Ca and other variables were observed (Table 1).

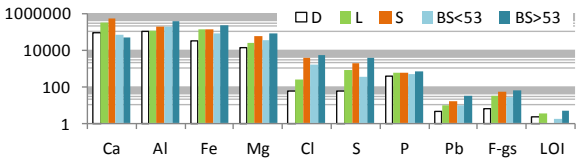

Fig. 1. Average values of characteristic variables in sediments of Nemunas River delta (D), Curonian Lagoon (L), Klaipėda Strait (S) and Baltic See (BS<53 - below 53 m depth, BS>53 - over 53 m depth). Ca, Al, Fe, Mg, Cl, S, P and Pb expressed in ppm, F-gs and LOI - in %.

Table 1. *p* values ($p<0.01$) of Spearman rank test of Ca inter-element correlation in the different parts of transitional system.

Nemunas River delta: (Mg, Ga)$^{nE-05*}$ (S, Sr, Rb)$^{nE-03}$
Curonian Lagoon: (S, Br)$^{nE-04}$ (Sr, Ni, V, Cu, F-gs, Pb, LOI, Zn)$^{nE-03}$ -Si^{nE-4}
Klaipėda Strait: (Mn, F-gs)$^{nE-17}$ Sr^{nE-15} Br^{nE-11} Cl^{nE-10} Mg^{nE-09} (Th, Ni)$^{nE-08}$ Na^{nE-07} (Ti, Nb, Fe)$^{nE-06}$ (Ga, P, S, Cr)$^{nE-05}$ (As, Zn)$^{nE-04}$ (V, Pb, Co, Al, U, Cu)$^{nE-03}$ -Si^{nE-15}
Marine areas up to 53 m depth (B<53): Mg^{nE-07} LOI^{nE-05} Mn^{nE-04} (Cr, V, F-gs, Nb, Ti, Co, Zn)$^{nE-03}$ -Si $^{nE-4}$
Marine areas from 54 to 120 m depth (B>53): (P, Nb)$^{nE-05}$ (Ti, Mg, Sr)$^{nE-04}$ (V, Cr, K, Al, Rb, Fe, Ga)$^{nE-03}$
* *p*-values are in superscript, $p<0.01 = p < 1E-02$

Peculiarities of sedimentary environment have a great impact on Ca accumulation in sediments as well as differences in Ca biogeochemical links.

References: [1] N. N. Greenwood, A. Earnshaw. (1997) *Chemistry of the Elements. 2nd Edition*: p 108.