Influence of land use in small karst catchments on the chemical status of peloid sediments on the eastern Adriatic coast

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Introduction:

An indented coastline with numerous bays characterizes the eastern Adriatic. Some of them represent shallow marine depositional environments where organic-rich sediments accumulate. Investigations for balneological characterization of several localities along the Croatian coast have shown that these organic-rich sediments may be classified as healing mud, i.e. peloids[1]. Most of the cathment areas supplying water and mineral mater to the Adriatic bays with peloids are affected by various degrees of human impact. In order to assess the most recent record of lithogenic and anthropogenic inputs to the Morinje and Makirina bay sediments (peloids) in central Dalmatian coast concentrations of both lithogenic (Al, Ti, Ca, Sc, Zr, and La) and potentially toxic elements (Mo, As, Cu, Pb, Zn) concentrations were analyzed cores and surface sediments, as well as catchment topsoil. The aim is to (1) characterize the sediments in terms of peloids and balneotherapy; (2) to determine the trace element/metal distributions in regard to mineral composition and to separate lithogenic and anthropogenic influences and to understand their potential remobilization; and (3) give an evaluation of pollution of sediments from the supplying catchments and its effect on their potential balneotherapeutic application.

Methods:

Geochemical, mineralogical, palynological, sedimentological and analysis of sediments and soil as well as geomorfological and geochemical modeling of the catchment with with GIS was performed at the two pilot sites Morinje and Makirina bay. For characterizing the probable anthropogenic inputs of heavy metals was evaluated by calculation of enrichment factors (EF) for these elements using Sc as the conservative element[2,3]. Mobility of metals was assessed by application of the first step (0.11 mol dm^{-3} CH_3COOH) of the harmonized BCR three-step sequential extraction procedure[4].

Results and Discussion:

The distribution and abundance of Cu, Pb and Mo were fond to be most interesting in the studied sediments. Pb is mainly supplied to the bay sediments by road runoff during rainy. Copper is supplied to the bays also during storm flow from the hinterland catchments. Since Cu is a part of soluble agrochemicals applied in the vineyards and orchards. In the studied sediment cores Mo increased (from 4.5 to 43 mg/kg) with increasing depth. The greatest accumulations of Mo occurred below the sediment–water interface where a source of Mo (inflow of drainwater) and low redox status coexist. Two distinct layers are produced in the sediment: an oxidized surface layer and underlying reduced layer where dissolved oxygen and other oxidized substances (e.g., Mn^{4+}) are absent. Two probable mechanisams are responsible for natural Mo accumulation of the formation of MoS_2 or tetrathiomolybdate which may form covalent bonds to Fe and Al solids and organic matter. Anthropogenic enrichment in Cu, Pb and Zn was evaluated through the calculation of the enrichment factors (EF). A moderate (EF's between 2-3.5) input of anthropogenic Cu and Pb is present between 0 and 10 cm sediment depth while below 15 cm the EF's have a natural variation (<2). Only a slight enrichment trend detected for Zn.

Since the analysed sediments are used as marine healing muds and various components of mud, particularly trace elements could be absorbed through dermal contact[5], the study of the abundance of potentially toxic elements as As, Pb, Hg, Cd, Se, Sb, Cu, Mo and Zn in healing mud is necessary to know their mobility to avoid possible intoxications. The potential metals (and other pollutants) released into coastal environments can limit the use of these environments for therapeutic purposes and indicator threshold values should be set if sediments are to be used as healing mud.

References: [1] Šparica et al. (2005) *Geol. Croat.* **58(1)**:21-72; [2] Shotyk et al. (2001) *Geochimica et Cosmochimica Acta* **65**(14):2337-2360; [3] Van der Weijden (2002) *Marine Geology* **184**(3-4):167-187; [4]Sutherland & Tack (2002) *Anal.Chim.Acta* **454**: 249-257; [5] Halevy (2001) *The Israel Medical Association Journal : IMAJ* **11**: 828-832.